THE MECHANISM OF HIGH PRESSURE OXIDATIONS OF ALIPHATIC ACIDS

Yakup Oner

NAVAL POSTGRADUATE SCHOOL
Monterey, California

THESIS

THE MECHANISM OF HIGH PRESSURE OXIDATIONS

OF ALIPHATIC ACIDS

by

Yakup Oner

Thesis Advisor: C. F. Rowell

June 1973

The Mechanism of High Pressure Oxidations of Aliphatic Acids

by

Yakup Oner
Lieutenant Junior Grade, Turkish Navy
B.S., United States Naval Postgraduate School, 1972

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL
June 1973

ABSTRACT

As a part of the study of the mechanism of high pressure oxidation of aliphatic acids, acetic acid solutions of 0.1 and 0.05 Normality were oxidized. Reaction conditions were selected as 200°-250°C and 1000 - 1500 psig for zero, one-half, one, two and four hour oxidation periods. No oxidation was observed at the end of several reactions without a catalyst. As high as 80% oxidation was observed from the oxidation for four hours at 250°C under 1500 psig of total pressure with Chromel-Constantan thermocouple wire (15 cm) as catalyst in the reacting solution. Increasing temperature showed an increasing reaction rate, while increases in pressure and decreases in concentration showed a decreasing effect on the reaction rate.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure

ACKNOWLEDGEMENT

The author would like to thank Professor C.F. Rowell for his outstanding leadership and guidance. The author also thanks K.J. Graham, R. Edwards and R. Scheile for their help with the system set-up. Special gratitude is expressed to both the United States Navy and the Turkish Navy for the privilege of attending this school.

I. INTRODUCTION

Recently research related to pollution control has received a great deal of attention. Although engineers have constructed plants for treatment of industrial wastes and sewage sludge, the basic chemical processes, especially for wet-air oxidation, are not well understood. Nevertheless, approaches to pollution prevention have been promising although not yet keeping pace with growing industry and population.

The work of this thesis is considered part of the research concerning the mechanism of aliphatic acid-oxidations at elevated temperatures and high pressures. The investigation has included use of substances that act as catalysts and give a higher oxidation rate with reduced cost. The former approaches to this problem have been to use the transition elements as catalyst. We have tried to approach the problem by simply using the oxidation potentials of substances in their various oxidation states. The oxidation-reduction potential of oxygen to reduce it from 0 to -2 oxidation state is 1.229 volts (Latimer, 1952). It is also known that thermocouples produce voltage across the tips corresponding to the applied temperature. There is no doubt that this junction voltage is not in the same sense as the oxidation-reduction voltage. Some possibility for using that potential as catalyst and thus obtaining the oxidation was thought to exist. Fortunately, results of our work have indicated that the potentials obtained do help in the solution of the problem. Certainly this is just the beginning for the idea of application to the problem at that point. Further work may explore the scope of the application Chromel-Constantan thermocouple gives a high potential for the reaction temperature; it was, therefore, used in this study.

II. HISTORICAL

As population increased problems of environmental impact arose, and people have had to protect their environment. One of the problem areas was "Water Pollution" as it still is today. Sources of pollutants have increased by the rapid growth of industry which goes back to 5000 B. C. Primitive man started his work on pottery near water sources thereby polluting them; by 2000 B.C. we see the Egyptians and Babylonians with great industrial plants, as compared to that time.

Big increases of industry and pollution can easily be observed, especially in the Eighteenth century and the Nineteenth century, and are still growing very rapidly and seriously now. In the Eighteenth century, French scientists obtained drinking water from sludge by chemical and physical treatment, which is an early example of pollution control. In the Twentieth century almost all nations of the world must fight with it.

The most important pollutants are organic and inorganic industrial wastes. Among them, carbonaceous materials give some organic acids when oxidized by nature. The oxidation products of those materials were studied in the laboratory as reported by R.C. TOMARELLI (1939). Oxidations of cokes, coal and pitches were carried out in aqueous alkaline permanganate and nitric acid solutions at temperatures from 100^{o}C to 250^{o}C under 7 to 25 atm. partial pressure of oxygen. Catalysts were investigated and the most effective ones were found to be cobalt salts and copper. His experiments showed that approximately 50 percent of these carbonaceous materials can be converted to water-soluble acids and the rest to carbon dioxide under proper conditions. Oxalic acid was one

of the major products among others such as trimellitic, pyromellitic, prehnitic and terephthalic acids.

Water soluble carboxylic acids were obtained from oxidation of coal by N. W. FRANKE and coworkers (1952). In acid media and high temperatures high yields of carbon dioxide and smaller yields of carboxylic acids were obtained. But in alkaline sokutions higher yields of carboxylic acids were obtained. Mesomorphic forms of carbon gave good yields of aromatic polycarboxylic acids. Aliphatic compounds have yielded carbonic and aliphatic acids. Reactions were carried out in a one liter autoclave with nitric acid; with alkaline permanganate; with sulfur trioxide; with nitric acid plus oxygen; and with oxygen in alkaline solutions. Each reaction was done for five hours at 250^{o}C and 750 psig. Standardized reaction conditions of 270^{o}C and 900 psig gave 70 percent aromatic acids of which one-third was observed to be benzenecarboxylic acid.

Other main pollutants are wastes from pulp and paper industry, and wastes from mining industry. To reduce the amount of waste from pulp and paper plants, "Mechanical Steam Aeration" facilities have been tried experimentally starting in 1943 at Wisconsin, as reported by L.F. WARRCK (1947). Studies have indicated that oxygen demand can be reduced 60 percent at that time. H.R. MURDOCK (1952) points out that toxic substances like sodium chloride, sodium carbonate, sodium sulfate, sodium hydroxide, sodium thiosulfate, hydrogen sulfide, ethanol, and crude tallow soap found in kraft waste water are more lethal to fish life than is B.O.D. J.S. MITTCHEL (1956) and W.M. FASSEL Jr. (1962) have studied the effect of mining and extractive metal industry on pollution. Cobalt recovery plants cause problems in operation with end wastes including

soluble chemicals. Considerable amounts of metallic salts remain in solution in the waste liquors and includes acids from leach and extraction operation. Those type wastes include toxic metals and caustic soda in solution.

Antipollution plants and methods have been arranged and developed in this century around the world. W.W. ECKENFELDER (1956) and C. M. COOPER (1944) have studied the design of aeration system for biological waste treatment and design variables of Agitated Gas-Liquid Contractors, respectively. F. ABEL, R.J. MORAN, and C.H. RUOF (1954) have accomplished a wet oxidation system for processing of sewage sludge by using a one liter nickel autoclave. Reactions were carried out in alkaline medium under total pressure of from 300 to 1000 psig at temperatures of 150°, 200°, 250°, and 300°C for two hours. At 150°C and 300 psig of oxygen, the percentage of initial carbon converted to carbon dioxide was about ten, but the odor was completely destroyed. At 250°C and 1000 psig initial partial pressure of oxygen, about three-fourths of original carbon was converted to carbon dioxide, and the product was colorless smalling like acetic acid (pH = 4.8). Increase in temperatures showed slight increase in carbon dioxide product.

ZIMMERMANN (1958) has reported 80 % of C.O.D. removal from sewage sludge by industrial plants and 95% oxidation of organic materials which cause pollution with reactor condition of 500-600°F and 1000-2200 psig. He also used raw materials as fuels in the plants and reduced the costs appreciably. Further modified mode of the ZIMMERMANN method has been started to work in Chicago, in 1964. Plant was designed for working temperatures less than 400°F and activated sludge was used, according to E. GUCCIONE (1964). G.H. TELETZKE (1964) has further modified the

ZIMMERMANN method to treat pulp and paper mill wastes and sewage sludges in Rothschild, Wisconsin.

E. HURWITZ, G.H. TELETZKE and W.B. GITCHEL (1965) observed that very little C.O.D. reduction occurs in one-hour oxidation period below 150°C for oxidation of sewage sludge, and increasing oxidation with increasing temperature. Temperature above 220°C was needed to achieve reduction range of 80% C.O.D. of the oxidized liquor increased with increasing oxidation reaching a maximum between 20 to 50% C.O.D. reduction, and decreased with increasing oxidation. At about 80% C.O.D. reduction, the amount of organic matter remaining insoluble was negligible.

In South Milwaukee a batch-type Zimpro Wet-Air Oxidation unit began to operate in 1964 with reaction conditions of 370-400°F and 500 psig, costing $ 38.18 per batch, and about 80% reduction in C.O.D. was achieved by R.W. NICHOLSON, D.J. PEDO, and J. MARTINEK (1966).

Components of sludge and its wet-air oxidation products were analyzed by G.H. TELETZKE and coworkers (1967) and have been reported that free amino acids and amino acids condensed to polypeptides were found in samples. The other basic organic chemicals found in the sample were proteins, lipids, starch, cellulose, and phosphorous. Among these materials, the lipids were the most resistant at low temperatures and starch was the easiest to remove as reported by R.B. BROOKS (1968).

The increasing demand for improved methods of treatment and dewatering of sewage sludge has resulted in increased interest in the U.K. and U.S.A. Among these methods which particularly found application in the U.S.A. and U.K., vacuum filtration by the coil filter and Rotoplug sludge concentrators can be mentioned. The main interest in Germany was on the carbofloc process for conditioning the sludge by lime and carbon

dioxide treatment, and the use of centrifuges for dewatering in past two decades. The most interest and developments of processes in U.K. and U.S.A. were the Wet-Air Oxidation, Centrifuges and FS Disposal system. Those processes and developments were studied and have been widely discussed by J.D. SWANWICK (1968) and by R.B. BROOKS (1968) and (1970). The Wet-Air Oxidation process was selected for sewage treatment service in Levitown, Pa. because Wet-Air Oxidation process best met all of the authority's requirements. The plant has provided clean, dependable and efficient sludge disposal with a low cost of $ 12.00 for 3.65 Ton/day. There was no odor, fly ash or soot and no air pollution at the end of the process of the effluent because the operation was a closed system as reported by P.X. BLATTLER (1970).

In Britain, after almost a century of river pollution caused largely by industrial effluents, it was realized that some treatment of sludge was needed like other nations. The Public Health Act (1937), the River Board Act (1948) and the River Act (1951) extended the powers of the boards to require control of all new discharges to rivers and outlets. National policy also requires that local authorities make adequate provision for the conveyance and treatment of all industrial effluent in the district at their sewage works when extensions are being planned. Now Britain claims that their rivers are in better conditions than twenty years ago as reported by S.H. JENKINS (1970).

The biochemical oxidations of various organic volatile acids by activated sludge was investigated by T. SATO and T. AKIYAMA (1972). Percentage oxidation of acetates were 46.7 and 38.2 for two different experimental methods used by them, and substrate removal rate was 38.4 mg/ (h)(g) of sludge. It was indicated that acetic and other

volatile acids are decomposed by β-oxidation in accordance with the tricarboxylic acid cycle. No difference was observed among the oxygen uptake of sodium, potassium, calcium, and ammomium salts of acetic acid. It was also found that the volatile acid salts were utilized by activated sludge, but inhibition was present at high substrate concentration. Formate and acetate was added simultaneously; there was no interaction between them.

Since sewage sludges include organic acids, in which the most resistive type for oxidation are saturated aliphatic acids, the oxidation of these were accomplished to seek understanding of the mechanisms of oxidation processes. The kinetic studies were done by using transition metals and/or their salts as catalysts. A.A. CLIFFORD and W.A. WATERS (1965) have studied the linetics and products of some carboxylic acids oxidizing by cobaltic salts and further, gave a nechanism which oxidations occur by an inner-sphere mechanism, as follows:

$$R{\cdot}CO_2H + Co(H_2O)_6^{3+} \overset{K_1}{\rightleftarrows} \{R{\cdot}CO_2Co(H_2O)_5\}^{2+} + H^+ + H_2O$$

and the rapid reversible formation of the cobaltic complex which then breaks down slowly with the formation of free radical;

$$\{R{\cdot}CO_2{\cdot}Co(H_2O)_5\}^{2+} \rightarrow R{\cdot} + CO_2 + Co^{2+} + 5H_2O$$

$$R{\cdot} + Co^{3+} \rightarrow R^+ + Co^{2+}$$

$$R^+ + H_2O \rightarrow R{\cdot}OH + H^+$$

$$R{\cdot}OH + Co(H_2O)_6^{3+} \overset{K_5}{\rightleftarrows} R{\cdot}O{\cdot}Co(H_2O)_5 + H_2O + H^+$$

This mechanism is similar to the oxidation of alcohols deduced by D.G. HOARE and W.A. WATERS in (1962) and (1964), and attributes relative ease of oxidation of acids to the fact that K_1, for complex formation with acid is much higher than K_5.

Direct electron transfer mechanism was suggested by W.F. BRILL (1960); P.J. ANDRULIS and coworkers (1966); T. MARIMOTO and Y. OGATA (1967); K. SAKOTA, Y. KAMIYA and N. OHTA (1969); E.I. HEIBA and co-workers (1969); A. ONOPCHENKO, J.G.D. SCHULTZ and R.SEEKIRCHER (1971); & T. ARATANI and M.J.S. DEWAR (1968) for the oxidation of aromatic substrates by Co(III) or Mn(III) at low temperatures (100^{o}).

Radical mechanisms have been suggested by D.A.S. RAVENS (1959); A.S. HAY and H.S. BLANCHARD (1965); C.E.H. BAWN and T.K. WRIGHT (1968) for the bromide promoted cobalt, or by E.K. FIELDS and S. MEYERSON (1968) for manganese catalyzed oxidations, and for cobalt or manganese acetate catalyzed oxidations of isopropyl-benzenes at 130-150^{o} by R. VAN HALDEN (1961).

The oxidation of alkyl aromatics has been studied by J.A. HOWARD and K.U. INGOLD (1967) and the individual termination and propagation rate constants have been measured for the xylenes, toluene, ethylbenzene, cumene and some other alkyl aromatics. Relatively large termination reaction:

$$2\ ROO\bullet \xrightarrow{k_t} \text{Non-radical products} + O_2$$

was explained by H.D. HOLTZ (1972).

The rate accelerating effect in hydrocarbon oxidations of transition metal ions was studied and mechanism was given by A.E. WOODWARD and R.B. MESROBIAN (1953). It is:

$$ROOH + M^{2+} \rightarrow RO\bullet + OH^{-} + M^{3+}$$

$$ROOH + M^{3+} \rightarrow ROO\bullet + H^{+} + M^{2+}$$

C. WALLING (1969) has pointed out that the rates of some commercial oxidations of alkyl aromatics are in excess of limiting rates predicted by

a kinetic rate. Usual propagation rate step given by

$$ROO\cdot + RH \xrightarrow{k_p} ROOH + R\cdot$$

was thought to be unimportant.

E.J.Y. SCOTT (1970) suggested the reaction:

$$ROO\cdot + Co(II) \rightarrow RCHO + Co(III) + OH^-$$

as major path for the oxidation of Co(II) to Co(III).

Free radical mechanisms have been suggested, involving the initial abstraction of H from the alkyl aromatic by some species such as Br, Cl, RO·, $RO_2\cdot$ and complete data was presented in Free Radicals In Solutions, by C. WALLING (1957) for the liquid phase chlorination at 80°C. According to H.D. HOLTZ (1972) the use of chlorine catalyst results in C-C bond cleavage during the oxidation. These phenomena can be explained by radical mechanisms involving a chloride ion to chlorine atom chain. As we have observed from the history of oxidations of aromatic alkyl and aliphatic acid, mechanisms seem not perfectly clarified.

III. EXPERIMENTAL

A. SYSTEM DESCRIPTION

A one-liter capacity stainless-steel reaction vessel with a gauge mounted on top of it was put into an electrically-heated controlled furnace. A copper ring served as coupling between reaction vessel and base of gauge, to prevent any oxygen leaking out of the system. A bolt was used to hold the vessel in the furnace through the bottom of the furnace and into the base of the vessel. Thermocouple readings were taken by putting the thermocouple wires (Iron-Constantan) through a hole in the bolt, so that the top of the thermocouple was in contact with the reaction vessel and this contact was established by a cavity with a depth of 0.75" which provided a temperature reading as close as the temperature inside the reaction vessel that has been subjected to oxidation.

A 24-gauge Iron-Constantan couple was used as thermocouple during the entire operation. Voltages corresponding to temperature of the solution inside reactor were measured using a Leeds and Northrup Temperature Potentiometer. Another temperature indicator on the furnace agreed with the thermocouple within $\pm 2^{\circ}C$ which it showed the temperature of the inside surface of the furnace. A Variac was used to set the reaction temperature, and it also served as remote control console with two circuit-breaker toggle switches on it for heater and autoclave, respectively. Mixing was based on a rocking motion of the whole set about a horizontal axis.

A 100 ml capacity glass-bottle was used as reaction-bottle and also to reduce the probable effect of steel on reaction kinetics. A hole

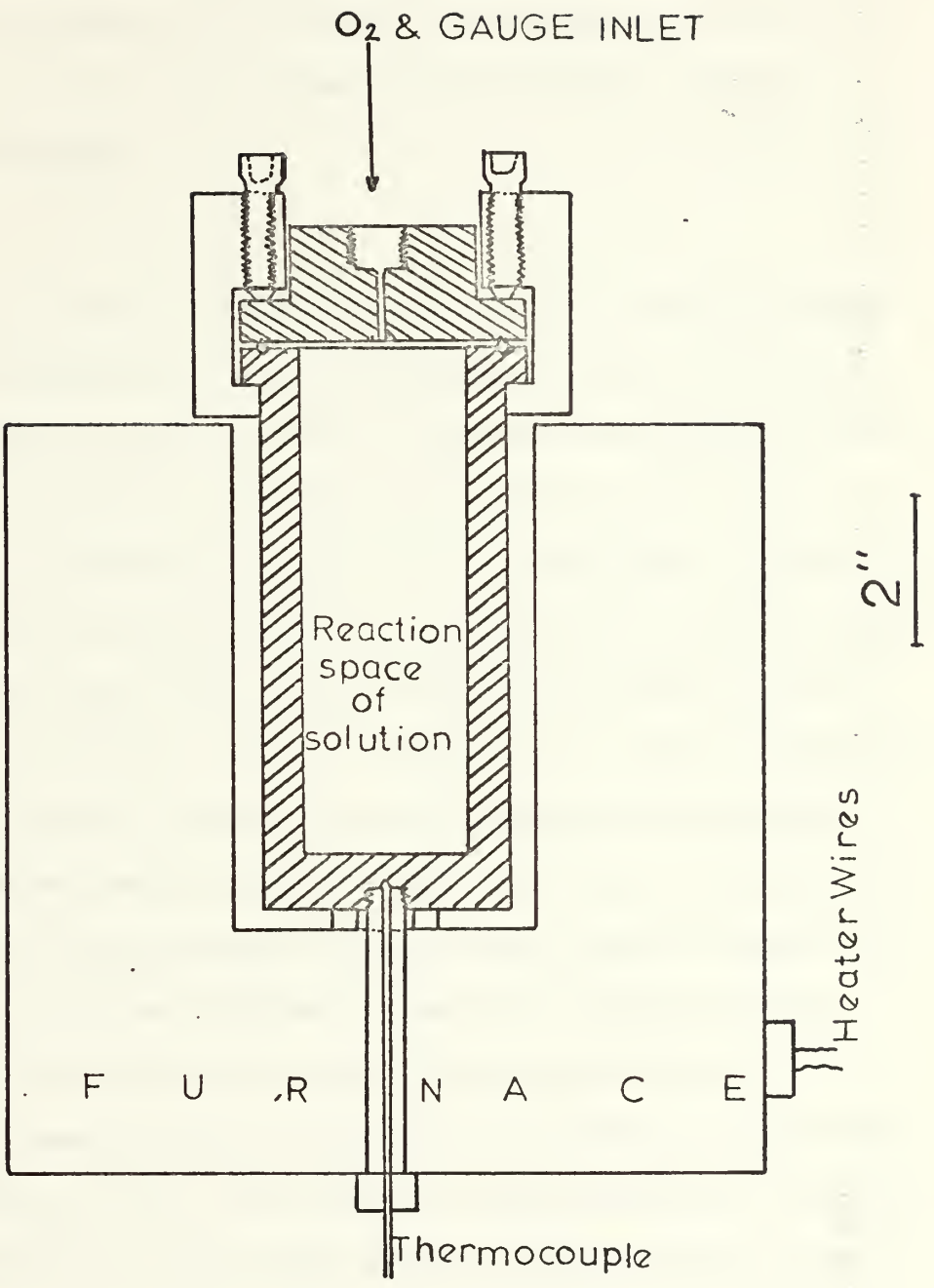


Figure 1
SYSTEM DIAGRAM

near the top of the bottle was the only way for oxygen to get in contact with solution to be oxidized. The system was completely closed from the beginning of heating to the cooling to room temperature, so that there was no oxygen flow in and out during the entire process after oxygen was brought into contact with the solution. Figure 1 shows system circuitry.

B. PROCEDURE

0.1 and 0.05 N Acetic acid solutions were made by diluting glacial acetic acid volumetrically, and was standardized against 0.1 N sodium hydroxide standard solution. 100 ml of this solution was put into reaction bottle for oxidation, and the system was filled with oxygen to various initial pressures for selected reaction conditions. The initial pressure values were calculated in such a way that, when desired temperatures were reached the total pressures needed were obtained for each designed reaction series. Ideal Gas Law was used to calculate values of pressures for reaction condition that was specified by temperature, pressure, time and concentration of acetic acid. The corrections were needed because of the non-ideality of air, water vapor and oxygen gas. Several test runs were accomplished to haveethose corrected initial pressure and to have variac setting for design temperatures.

The vapor pressure of water was obtained from Physics and Chemisty Handbook, 46 ed., p. D-144. That value of vapor pressure was taken for the entire solution as a very small amount of acetic acid was present. By combining this information and knowing the final pressure desired, the desired initial pressure of oxygen was calaulated.

Heating was started after letting pressurized system stand one hour, so that it could be possible to discover a leak if there was any.

It was also necessary to wait for the pressure to stop rising at the end of heating even after reaching the desired temperature. This is due to the effect of heat transfer into the solution from the vessel wall. When any small leak was observed the filling procedure was repeated. The shaking system was started after all these conditions were stabilized. Temperature and pressure were recorded at time periods during the autoclaving.

Switches corresponding to heating and shaking were turned off simultaneously right after the end of the shaking period in order to cool the system. There was no special effort made to cool the system such as air ventilation, and the hood in the room was held "On" position for the entire operation. The cooling to room temperature takes about ten to twelve hours depending on the reaction temperature that was used. The system was opened when it was at room temperature after cooling.

C. ANALYTICAL METHODS

Each reactant and product were analyzed by four different methods in order to find the amount of acetic acid oxidized. 10 ml of each (reactant and product) solution was neutralized by 0.1 N NaOH standard solution so that a quantitative value about the amount of axidation was obtained for each reaction. Phenolphthalein was used as indicator to determine the end point for each titration. Generally three titrations were carried out for every sample, and the result was averaged.

Chemical Oxygen Demand (C.O.D.) was determined for reactant and for every product at the end of each run. Dichromic acid method with Ag_2SO_4 catalyst was used for determination of C.O.D. as described in Standard Methods (1965).

Gas-liquid chromatograms were obtained on a Bendix G.C. Chromalab Series 2200 and a thermal conductivity (T.C.) detector was used for this analysis. The column that was used was packed with 20% FFAP (DMCS treated) on 70/80 mesh Chromosorb W, 8' x ¼" in size. No re-conditioning was necessary before each use of the column.

A Beckman pH meter was used to measure the pH's before and after the reaction.

IV. RESULTS

A. ACID-BASE TITRATION RESULTS

The results of acid-base titrations before and after the oxidation are as shown in Table I.

The titration results for products under the conditions of 250°C, 1500 psig 0.1 N acetic acid oxidations showed that the maximum acidity removal was 66%, whereas the maximum removal value was 76% for the products that have been obtained under the conditions of 250°C and 1000 psig with 0.1 N acetic acid oxidation. This is the indication that the increase in pressure decreases the rate of oxidation for periods of oxidation that were longer than one hour. The products that were obtained after one hour oxidation of acetic acid (0.1 N) at 250°C for both 1000 psig and 1500 psig of total pressure gave almost the same percentage of acidity removal. The difference between the two values was so small that it is assumed to be the result of experimental error. The increase in pressure showed that increase in reaction rate for the reactions that have the periods of oxidations less than one hour. This is observed from figure where the removal of acidity for 1500 psig as percentage is almost twice the value that was obtained for 1000 psig for both having the oxidation periods of zero hours. After one hour oxidation the situation was reversed.

The oxidations for the conditions of 200°C, 0.1 N, 1000 psig and 200°C, 0.1 N, 1500 psig was not as complete as the cases of 250°C. As observed from Table I and from figure 2, the oxidation of 0.1 N acetic acid gave as high as 21% acid removal under the condition of 200°C and 1500 psig. But this set of reactions was done by raising the temperature

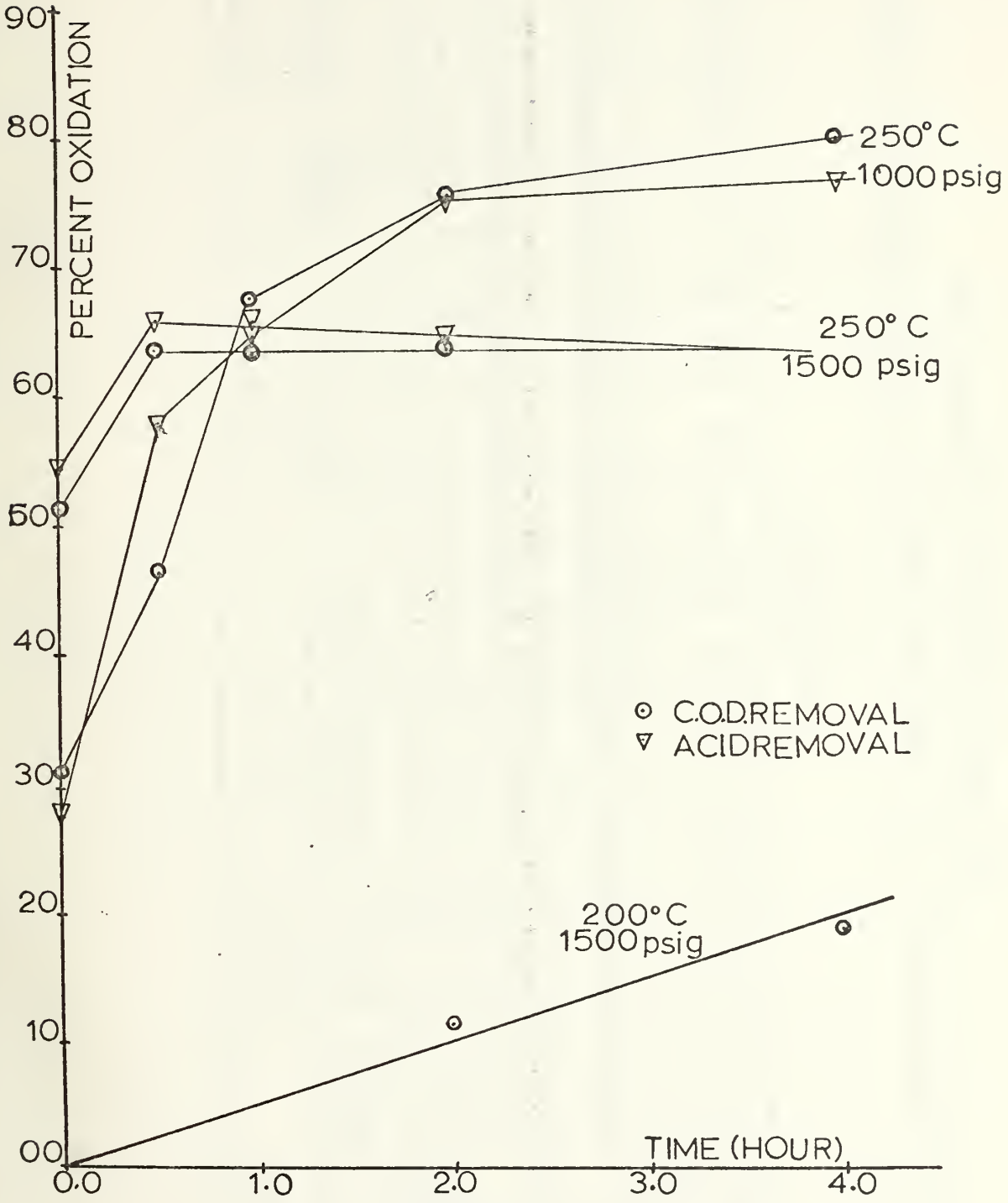


Figure 2

Percent oxidation of acetic acid with time

Reaction Condition	250°C , 0.1 N									200°C , 0.1 N					250°C 0.05 N		
	1500 psig				1000 psig					1500 psig			1000 psig		1500 psig		
Reaction Time(Hr)	0.0	0.5	1.0	2.0	0.0	0.5	1.0	2.0	4.0	1.0	2.0	4.0	1.0	2.0	0.5	1.0	2.0
Initial Acidity	0.101	0.101	0.101	0.101	0.101	0.101	0.101	0.108	0.101	0.106	0.106	0.106	0.101	0.106	0.05	0.05	0.05
Final Acidity	0.046	0.034	0.034	0.036	0.073	0.043	0.035	0.027	0.024	0.089	0.085	0.084	0.098	0.096	0.031	0.025	0.026
Percent Oxidation	55.	66	66	65	28	57	65	75	76	16	20	21	3	9.4	38	50	48

TABLE I

Acidities(Normality) of reactant and product based on titration by NaOH(Sodium Hydroxide)

before the start of oxidation-shaking to 220°C and then reducing to 200°C and at that point shaking was started. In order to understand the temperature effect better, the reaction series with 200°C, 1000 psig, 0.1 N acetic acid oxidation was completed by not allowing the temperature to rise to more than 200°C and very low oxidation was observed.

The oxidation products under the reaction conditions of 250°C, 1500 psig, 0.05N of acetic acid showed that the decrease of concentration of acetic acid decreases the rate of oxidation.

No oxidation was observed at the end of several reactions without catalyst. The best value that have been observed was about 3% oxidation which is within experimental error.

B. CHEMICAL OXYGEN DEMAND ANALYSIS (C.O.D.)

The same method that was described in Standard Methods was used for each reaction to make C.O.D. determinations. It was necessary to have Ag_2SO_4 as catalyst in H_2SO_4 solution to determine the C.O.D. Many attempts to determine the C.O.D. without Ag_2SO_4 failed and by using 4.90 grams of Ag_2SO_4 in each 2 lb. H_2SO_4 bottle, very good and reproduceable results were obtained. One or two days were required to get Ag_2SO_4 dissolved in the H_2SO_4. Reflux periods of 110 minutes were applied for each C.O.D. determination. In order to get consistent results, it was necessary to use the same kind of flasks, condensers for reflux and electrically heated hot plates. The results of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ titrations gave accurate results coinciding within the range of 0.10 ml difference. The inconsistent values outside this limit were discarded for the sake of accuracy. Same reflux ratios were obtained by using 650 watt hot plates.

Reaction Condition	250°C , 0.1 N									200°C , 0.1N					250°C, 0.05 N		
	1500 psig				1000 psig					1500 psig			1000 psig		1500 psig		
Reaction Time(Hr)	0.0	0.5	1.0	2.0	0.0	0.5	1.0	2.0	4.0	1.0	2.0	4.0	1.0	2.0	0.5	1.0	2.0
Initial C.O.D.	5.99	5.99	5.99	5.99	5.99	5.99	5.99	6.52	5.99	6.28	6.28	6.28	5.99	6.28	3.14	3.14	3.14
Final C.O.D.	2.93	2.17	2.173	2.2	4.62	3.24	1.97	1.6	1.25	5.56	5.56	5.23	—	6.06	1.912	1.595	1.591
Percent Oxidation	51	64	64	63	23	46	57	75.5	79	15	16	17	—	3.5	39	49	49

TABLE II

Chemical Oxygen Demand (gr/lt) values before and after each reaction and per cent oxidation

The C.O.D. analysis results for each reactant and products are as shown in Table II. The percent C.O.D. removal vs. time (hr.) curves are as shown in figure 2. The curves on that figure showed the same trend as the curves for acidity removal. Generally the C.O.D. removal was less than the acidity removal. This was thought to be the effect of imperfectly cleaned glassware, personal and systematic error, and some possibility of some oxides of catalyst metals during the process rather than forming 100% carbon dioxide and water. The close fittings of curves of acidity removal and C.O.D. removal is the indication of the possible reaction which is thought as

$$CH_3COOH + 2O_2 \rightarrow 2H_2O + 2CO_2$$

C. pH MEASUREMENT RESULTS

The pH values for each reactant and products were obtained by the Beckman Expandomatic pH meter and are shown in Table III. The increase in pH values were observed for each product of acetic acid oxidation for selected reaction conditions, which indicates that reactions had eliminated some of the acetic acid. It is difficult to have a good co-relation between the pH values and percentage of acidity removal. Values in Table III were checked from time to time in order to be sure that the errors in measuring were minimized.

D. GAS LIQUID CHROMATOGRAPHIC ANALYSIS (GLC)

The chromatograms were determined with a Bendix Chromalab Series 2200. The operating conditions were as follows:

Column:	coating	FFAP
	concentration	20% w/w
	support	Chromosorb W 70/80 mesh (DMCS)
	length	8'
	diameter	¼"

Reaction Condition	250°C, 0.1 N									200°C, 0.1N					250°C, 0.05 N		
	1500 psig				1000 psig					1500 psig			1000 psig		1500 psig		
Reaction Time (Hr)	0.0	0.5	1.0	2.0	0.0	0.5	1.0	2.0	4.0	1.0	2.0	4.0	1.0	2.0	0.5	1.0	2.0
Initial pH	2.85	2.85	2.85	2.85	2.85	2.85	2.85	2.74	2.85	2.75	2.75	2.75	2.85	2.75	3.0	3.0	3.0
Final pH	3.6	3.5	3.7	3.7	3.9	4.0	3.7	3.65	3.8	3.9	4.12	4.12	3.5	3.9	3.5	3.6	3.7

TABLE III

pH values of solutions before and after reactions

Reaction Condition	250° C 0.1 N									200°C 0.1 N					250° C 0.05 N		
	1500 psig				1000 psig					1500 psig			1000psig		1500 psig		
Reaction Time (Hr)	0.0	0.5	1.0	2.0	0.0	0.5	1.0	2.0	4.0	1.0	2.0	4.0	1.0	2.0	0.5	1.0	2.0
Initial GC	3.74	3.74	3.74	3.74	3.74	3.74	3.74	4.0	3.74	5.25	5.25	5.25	3.74	5.25	1.24	1.24	1.24
Final GC	2.24	1.33	1.02	1.04	2.36	1.22	0.73	0.81	0.68	2.96	—	2.61	—	3.19	0.8	0.73	0.91
Percent oxidized	40	65	73	72	37	67	80	80	82	44	—	50	—	39	36	41	27

TABLE. IV

Ratios of area of HOAc to area of H_2O times 10^3 on GC chromatograms before and after oxidation-reactions

Temperature: oven 150-165°C
inlet 200°C
detector 200°C

Detector: thermal conductivity

Carrier: Helium

Flow rate: 50 ml/min

Bridge Current: 225 ma

Sample Size: 5 1 for reactants
10 1 for products

Attenuation: 500 for water peaks of reactant sample
1000 for water peaks of product sample
10 for acetic acid peaks

The analysis of each sample injection took about 35 minutes. The water peaks appeared 1.2 minutes after injection, and the retention time for acetic acid was 5.4 minutes. In this analysis the substances that were observed were acetic acid and water. This indicates that there was no other substances produced in the oxidation process. The typical gas chromatogram is shown in figure 3 for this analysis. In order to obtain the extent of oxidation, the ratios of areas of acetic acid peaks to water peaks were calculated and are as shown in Table IV.

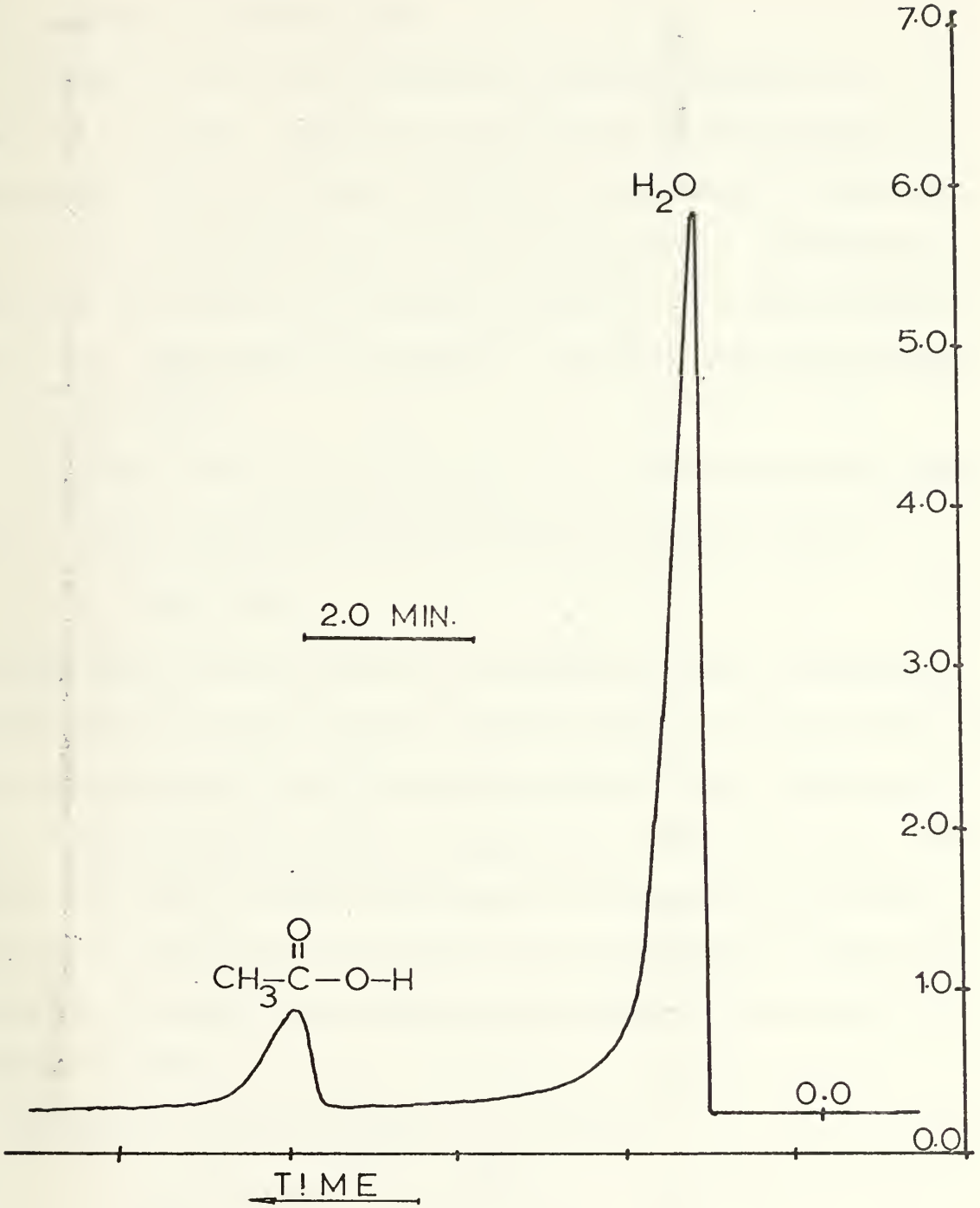


Figure 3
TYPICAL G.C. GRAPH FOR ACETIC ACID

V. DISCUSSION

A. CHEMISTRY OF ALIPHATIC ACIDS

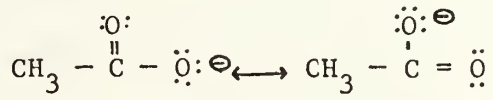
Aliphatic acids usually have high boiling and melting points, and are hard to oxidize. Oxidation of hydrocarbons can be established in a way that products are only CO_2 and H_2O. The oxidation of acetic acid can be described in the same way when it is successful. The hardness of oxidation of acetic acid is basically related to the internal effects of structure. These effects are inductive, resonance, polar and electronic structural effects.

In general, electron-donating groups on a molecule reduce the acidity of it. Methyl group has an electron-donating inductive effect of

$$\overset{+}{C}H_3 \text{---} C\bar{O}OH$$

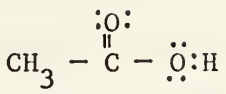
so that acetic acid is weaker than the inorganic acids. The electron cloud between CH_3 and C in acetic acid lies closer to the C=O carbon, and the electron cloud on the C–O bond lies closer to the O. The less electron density around the CH_3 and H makes them harder to oxidize. Less electron affinity of carbon with respect to hydrogen and the greater electron-donating effect of CH_3 with respect to hydrogen in acetic acid structure deactivates the carbon (on the α-position) with respect to radical oxidation.

Structure of acetate ion can be ascribed as:

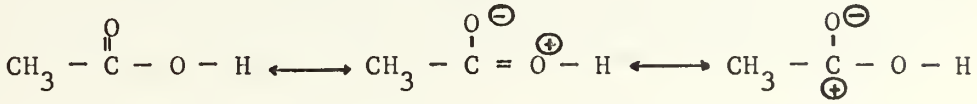


which posseses two bonds of one and a half order. By using the same method for acetic acid considering the addition of one proton to acetate

ion, the structure is then:



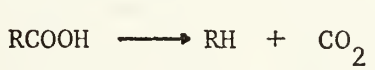
But interaction between electrons bonding to the two oxygen atoms still exist and molecule can be represented as hybrid structure of:



Because of different electron affinities of nuclei, the bonds that hold different kinds of nuclei together are polarized, and charge separation results with the appearing electron richness of one nucleus and electron deficiency of other, so that polarized molecules are very tightly held together. As shown by hybrid structure above, the delocalization of electrons lowers their energy, and the molecules with a number of resonance structures may be written are to be very stable (HAMMOND, G.C. and CRAM, D.J., 1959).

The carbonyl oxygen atom attracts electrons powerfully by both conjugative and inductive effects. —OH always acts as electron-donor with conjugative effect when conjugated to an electron-demanding center, so that the vibrational frequency is reduced by electron release from —OH which is 1717 cm^{-1} for acetic acid.(KOHNSTAM, G. and WILLIAMS, D.L.H., 1969). These facts assure the stability of acetic acid for oxidation.

Aliphatic acids can be decarboxylated during the oxidation process, if they have functional groups or double or triple bonds on the - or β- positions with the reaction;



In the acetic acid case the R is the methyl group and makes the decarboxylation harder by deactivation. However, the deactivation on acetic acid is at variance with the expected stability of the resulting radicals,

since they would be expected to be stabilized by resonance similar to allylic and benzylic radicals. The $CH_3^{\bullet}$ is nucleophilic and behaves differently than those (MARCH, J., 1968).

In early 1900 it was found that the decarboxylation reactions are bimolecular, and involve the undissociated acid. In 1930's the proposed intermediate in decarboxylation was the dipolar ion. but in 1941 this was invalidated.

Catalysts are used in reactions to accelerate the chemical reaction. Activation energy in a reaction gives the measure of rate of reaction. The catalyst affects the reaction in such a way that, the activation energy is much lower than that of the uncatalyzed reaction. By definition a catalyst is not consumed in the over-all reaction. Metal catalysts can serve either as homogeneous or heterogeneous catalyst in an organic reaction. A heterogeneous catalyst is one that supplies the surface for lowering the activation energy on which reactions occur. Metal ions in reactions as homogeneous catalyst can affect the reaction to lower the activation energy depending on the oxidation states and oxidation potentials between those states. Oxidation potentials for elements are given by LATIMER (1952). The homogeneous catalytic effects of metal ions are recently of great interest in research. Those ions are usually the heavy metal ions. They show the effect on the rates of radical chain autoxidations by reacting directly with the hydrocarbons and initiating the oxidation chains. Moreiver, they generate the radicals by reaction with hydroperoxide, as reported by WOODWARD, A.E. and MESROBIAN, R.B. (1953). The probable route of reaction series they reported include the steps (1) and (2), below.

$$ROOH + M^{2+} \rightarrow RO\cdot + HO^{-} + M^{3+} \quad (1)$$

$$ROOH + M^{3+} \rightarrow ROO\cdot + H^{+} + M^{2+} \quad (2)$$

This requires the metal ions to exist in two oxidation states with a suitable oxidation-reduction potential. These reaction are complicated since metal may be a complexed ion. According to C. WALLING (1957) reaction (1) is faster than reaction (2).

Oxidation of hydrocarbons is the main process for petrochemicals and products obtained from them. Oxidations could be complete combustion to CO_2 and H_2O or less complete to give intermediate products, and are highly exothermic for fuels when ignited from outside source. The mechanism of hydrocarbon oxidations involve radical formation and reactions. As a diradical, oxygen can abstract the hydrogen from hydrocarbon and produce hydroperoxy, peroxy, and carbon chain radicals. Those produced radicals again react with the oxygen and hydrocarbons to form orgaiic peroxides, organic hydroperoxides and other peroxy radicals with chain reactions. Organic hydroperoxides formed are especially very reactive for cleavage of the O-O labile bond homolytically and by reacting further to give final products. Radicals whivh are stable can react with oxygen at room temperature but unstable radicals need high temperature and initiator to react as in the case of acetic acid oxidation (NORMAN, L.A., et. al., 1971)

The presence of water in reaction medium helps the reaction, probably by forming very effective chain carrier radicals via the route:

$$RH + O_2 \rightarrow R\cdot + HOO\cdot$$

$$R\cdot + H_2O \rightarrow RH + HO\cdot$$

$$R\cdot + HOO\cdot \rightarrow ROOH \rightarrow RO\cdot + HO\cdot$$

$$RO\cdot + H_2O \rightarrow ROH + HO\cdot$$

and in terms of Haber-Weiss reaction scheme:

$$R\text{-}CH_2\text{-}OH + HOO\cdot \rightarrow R\text{-}\dot{C}H\text{-}OH + H_2O_2$$

$$R\text{-}CH_2\text{-}OH + HO\cdot \rightarrow H_2O + R\text{-}\dot{C}H\text{-}OH$$

$$H_2O_2 + M^{2+} \rightarrow M^{3+} + HO\cdot + OH^-$$

Since HO· radical is very good chain carrier, and the formation of it is preferred, the oxidation reactions in water medium by catalyst is facilitated.

B. CONCLUSION

The first order rate law was applied to data from analytical results, and $\ell n(C_t/C_o)$ vs t(hr) was plotted for each reaction series. Figures 4 - 18 show these graphs and rate constants. Since pH data was not suitable to plot it was not used in these drawings, and the k values for acid-base titration, gas chromatography, and chemical oxygen demand analyses were averaged and are shown in Table V.

Experiments showed that the uncatalyzed system did not give any oxidation for acetic acid at the temperatures up to 250°C, which is the upper limit of our study. As observed in figure 1 and from k_1 and k_2 values presented in Table V, the catalyzed system gives as high as 80% oxidation completed, and the rate is greatly affected. The plots in figures 4-18 show two different stages of oxidation with each obeying the first order law of reaction kinetics with respect to concentration of acetic acid. The rate on first stage is faster than that of the second period.

The effect of catalyst on the mechanism of oxidation is not well understood for this work from examining the kinetic data, but some predictions can be made. The solubility of copper metal in our solution

TABLE V

Reaction condition	k_1(av.)	k_2(av.)
0.1 N, 250°C, 1500 psig	0.71612 hr^{-1} (2.0×10^{-4} sec^{-1})	0.00367 hr^{-1} (1.0194×10^{-6} sec^{-1})
0.1 N, 250°C, 1000 psig	1.02924 hr^{-1} (2.9×10^{-4} sec^{-1})	0.23887 hr^{-1} (0.7×10^{-4} sec^{-1})
0.1 N, 200°C, 1500 psig	0.04736 hr^{-1} (1.3156×10^{-5} sec^{-1})	
0.1 N, 200°C, 1000 psig	0.09689 hr^{-1} (2.6914×10^{-5} sec^{-1})	
0.05N, 250°C, 1500 psig	0.54137 hr^{-1} (1.5038×10^{-4} sec^{-1})	~0.0

was observed in the early days of the study, with the blue color of product after a copper wire has been put into reactor to serve as holder for glass bottle. The concentration of Cu ions in solution was not determined, but no oxidation was found in that reaction which indicates copper did not work as catalyst or perhaps inhibited oxidation. Since the wire was not in the solution it is unlikely that it served as a catalyst. The catalyst in this study was Chromel-constantan thermocouple wire which includes Ni, Cu, and Cr in metallic form. The pale greenish color of the product solutions indicated that those metals did undergo conversion to ion in solution. If they were in ionic form during the reaction, homogeneous catalytic effects from they could be established. Cr and Ni are known as good catalysts and are widely used in such reactions.

Heterogeneous catalytic work might also be expected. The small values of rate constants in second periods could be the result of heterogeneous catalytic work such as the acetate ions and oxygen found enough surface on metals and undergoing oxidation in first period then the possible formation of metal oxides around the metals did not let the acetate ions find enough surface for oxidation after first period.

Another possible catalytic effect is the formation of junction potential across the wires and reducing the activation energy for transition state by the electromotive force and resulting in products with high value of oxidation. Iron-constantan wire was put into the reaction solution to serve as catalyst for oxidation at 250^{o}C. There was no oxidation obtained from that reaction, which is an indication that the possibility of catalytic behavior of iron-constantan either by homogeneous or by heterogeneous means was not realized.

Another explanation is that the potential produced by metal junctions in iron-constantan case could not pass the critical value to initiate the reaction. The possibility is enforced also by the result of reactions about 200°C and below with the chromel-constantan catalyst in contact with the solution. As a rough comparison, iron-constantan gives 13.553 mV at 250°C, whereas chromel-constantan gives 13.419 mV at 200°C. These values are so close that the catalytic effects of junction potentials seem to be important.

Either from the junction-potential or metal and metal ions catalytic effects, the temperature dependence of the reactions is obvious as observed from figures 1-3 and figures 4-18. As the temperature inreases the amount and the rate of oxidation increases.

The pressure dependency of reactions are not so obvious as it was for temperature. But as the pressure decreased at 250°C for 0.1 N acetic acid oxidation the increase in k_1 values oy a factor of about 1.5 was observed, and the period of time of first stage oxidation gets broader by a factor of about 2.0 for 500 psig.

The decrease in concentration affects the rate constants by showing a slightly decreasing k_1, but increase of k_2 by about 20 fold.

It is clear that our definition of "Zero-Hour" is not for the starting point of oxidation, but it is for shaking. Apparently oxidation is in progress during the start-up period as observed from figures 1 and 4-18. Oxidation probably continues during the cooling period, as observed from the oxidation at 250°C, 1000 psig, and 0.1 N acetic acid for zero-hour. That reaction was allowed to cool to the room temperature and was not opened for three days, so that 65% oxidation was found. The duplicate of same reaction showed 30% oxidation after regular time of cooling period applied (about twelve hours).

Mechanistic studies were done especially in last decade for aliphatic acid oxidations. CLIFFORD and WATERS (1965) proposed radical mechanism by metal catalysis as:

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}M(III) \rightarrow R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\cdot + M(II) \quad \text{(slow)}$$

$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\cdot \rightarrow R\cdot + CO_2 \quad \text{(very fast)}$$

C. WALLING (December 31, 1969) also proposed a radical mechanism which seems complementary to Clifford's proposal:

$$R\cdot + O_2 \xrightarrow{k_a} RO_2\cdot$$

$$RO_2\cdot + RH \xrightarrow{k_p} ROOH + R\cdot \qquad k_a \gg k_p$$

$$2\ RO_2\cdot \xrightarrow{k_t} \text{Inert products} + O_2$$

Direct electron transfer mechanisms have been suggested by HEIBA and coworkers (1969); ANDRULIS, et. al.; MARIMOTO and OGATA (1967); and in 1972. HOLTZ suggested that free-radical and direct electron-transfer mechanisms should not be very distinctive, since every chemical reaction involves electron transfer.

It is not possible to propose a mechamism based on the results of our kinetic study, but it is known that the stoichiometry of acetic acid oxidation is:

$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}H + 2O_2 \xrightarrow[\text{cat.}]{\Delta} 2CO_2 + 2H_2O$$

Regardless of the mechanisms proposed, it must now show that the presence of catalysis will make the oxidation of carboxylic acids possible, even though people have thought them to be very resistive to oxidation and used them as solvents in many catalytic oxidation reactions.

COD analysis of products of 0.1N Acetic acid oxidized at 250°C, 1000 psig.

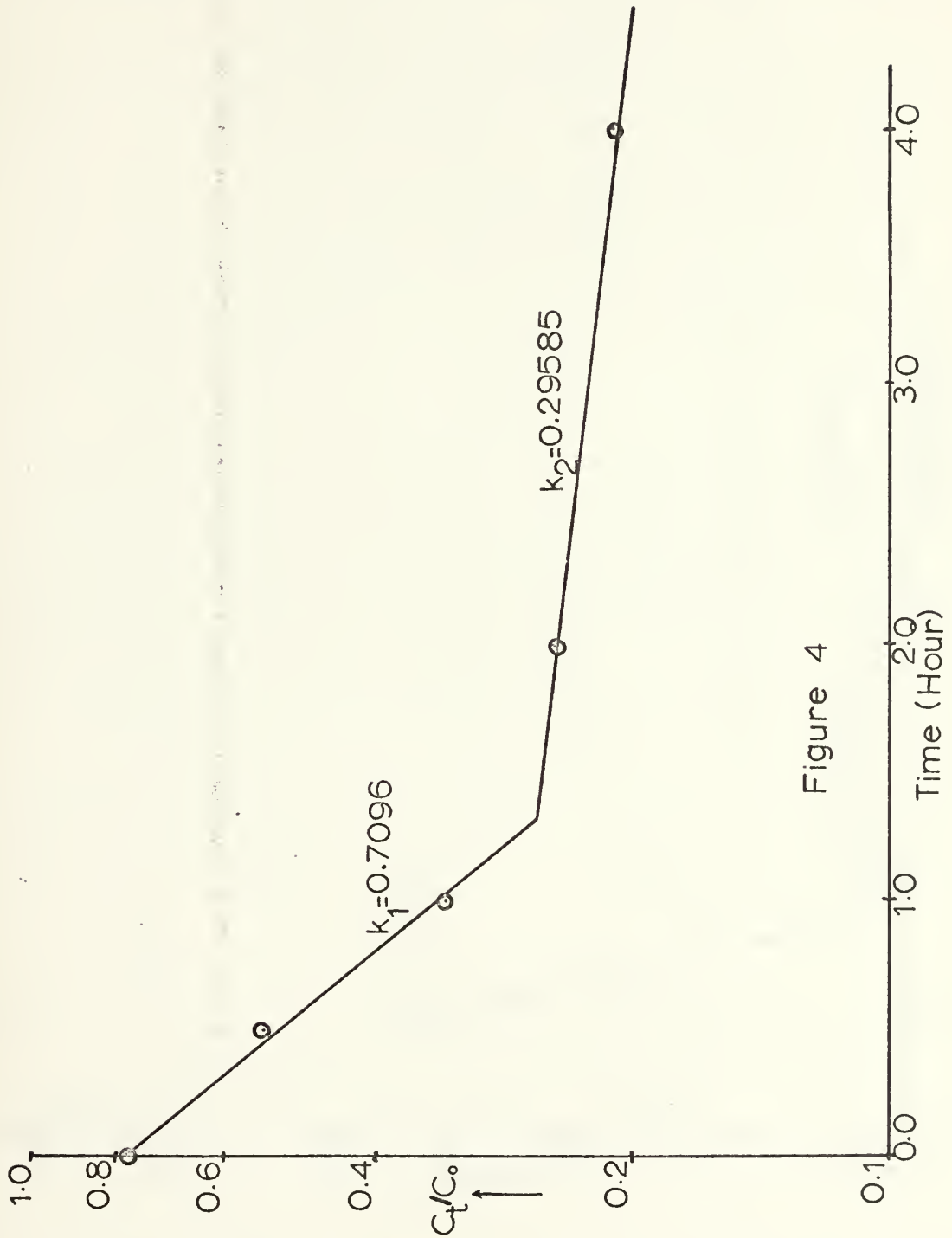


Figure 4

GC analysis of products of 0.1 N Acetic acid oxidized at 250°C 1000 psig

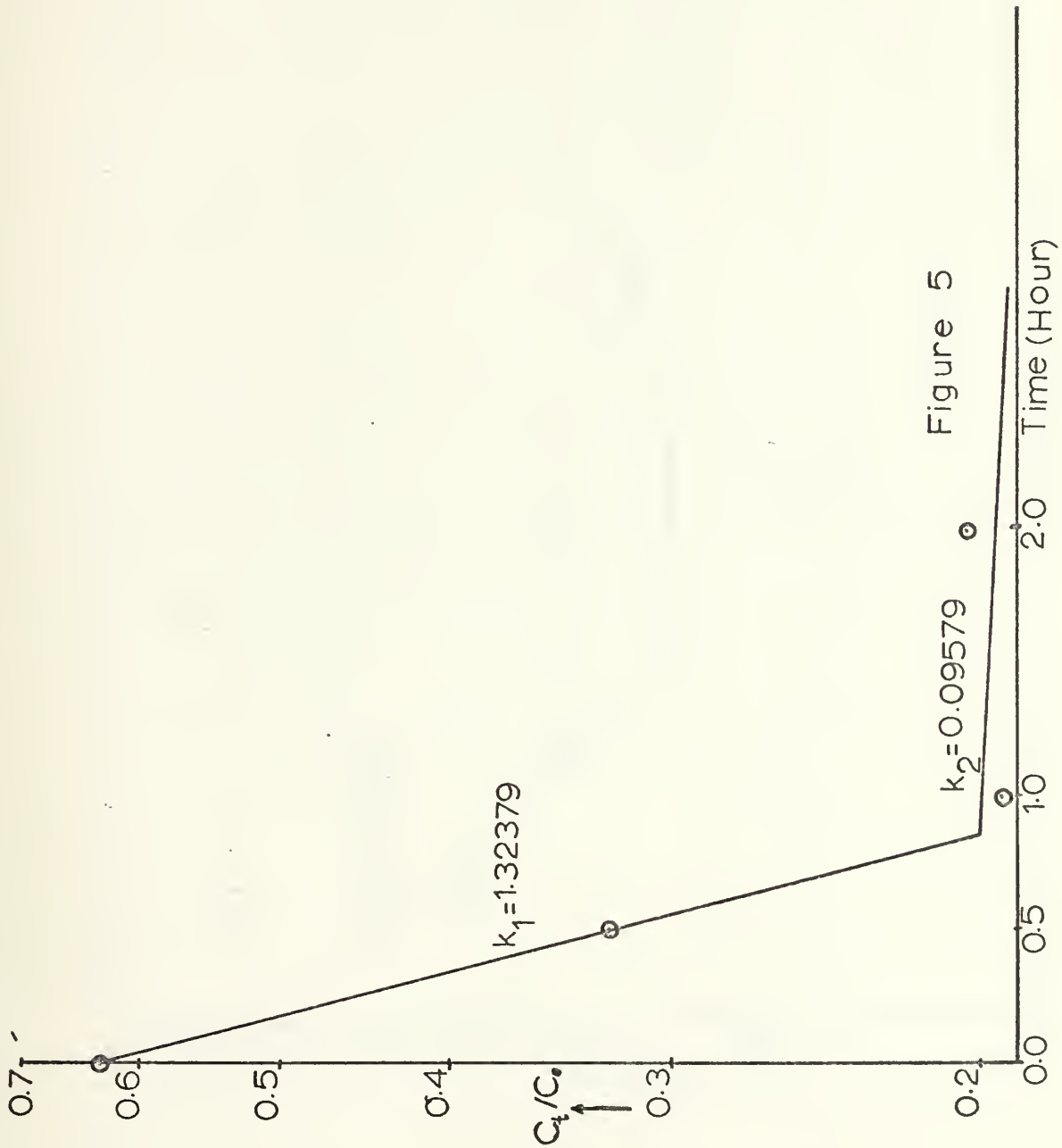


Figure 5

Acid-base titration analysis of products of 0.1 N Acetic acid oxidized at 250°C 1000 psig

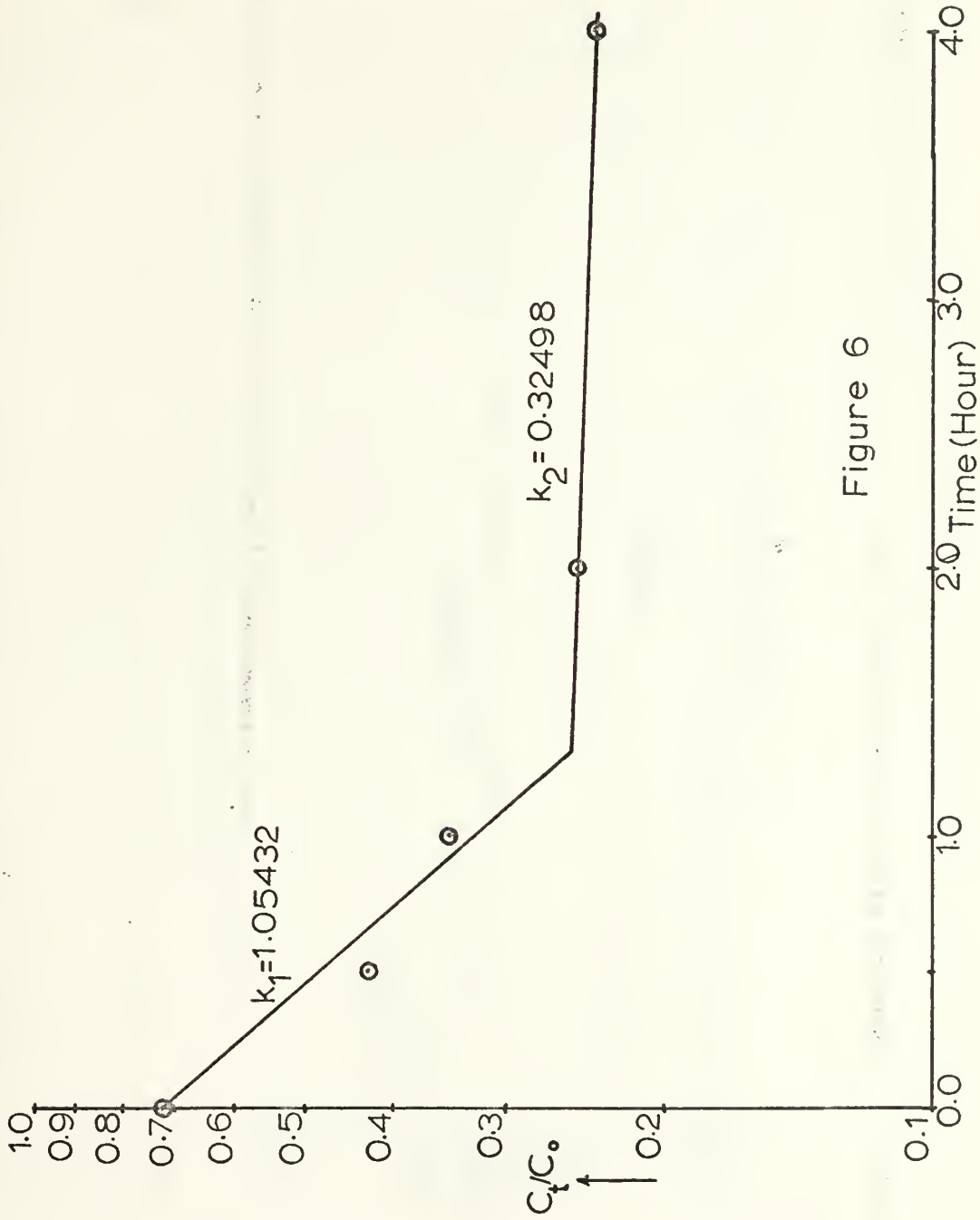


Figure 6

COD analysis of products of 0.1 N Acetic acid oxidized at 250°C, 1500 psig.

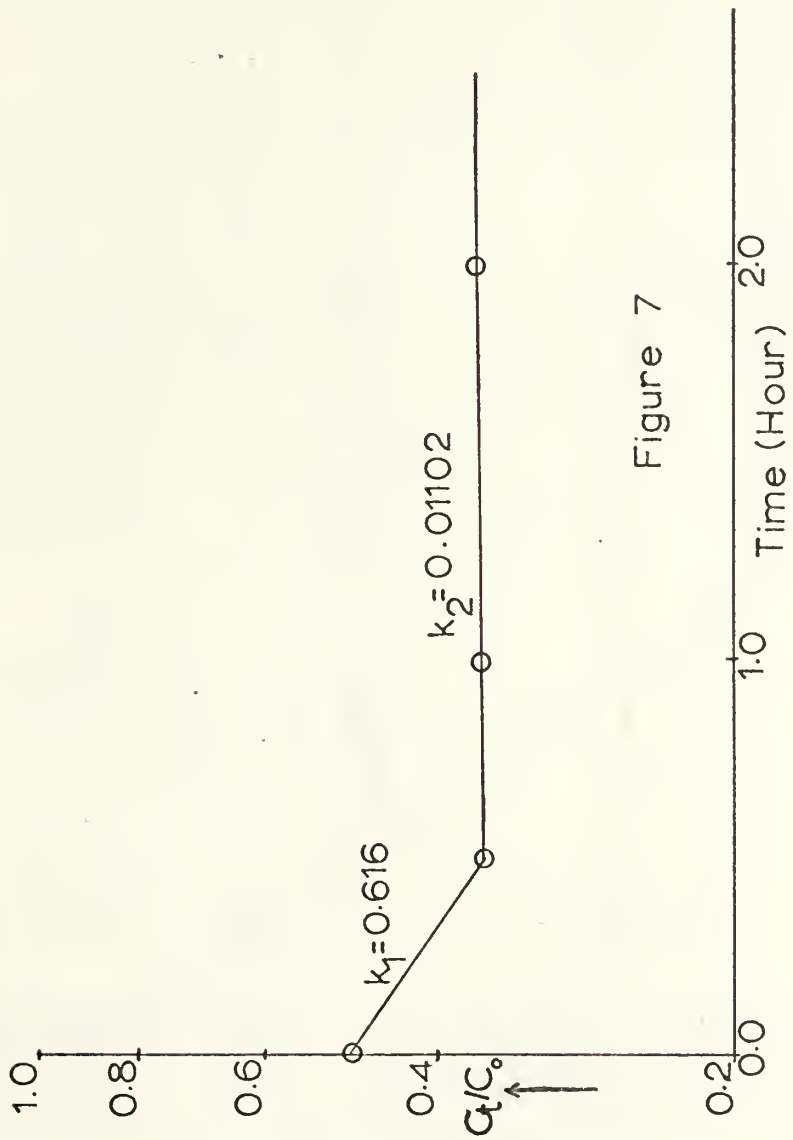


Figure 7

GC analysis of products of 0.1 N Acetic acid oxidized at 250°C 1500 psig

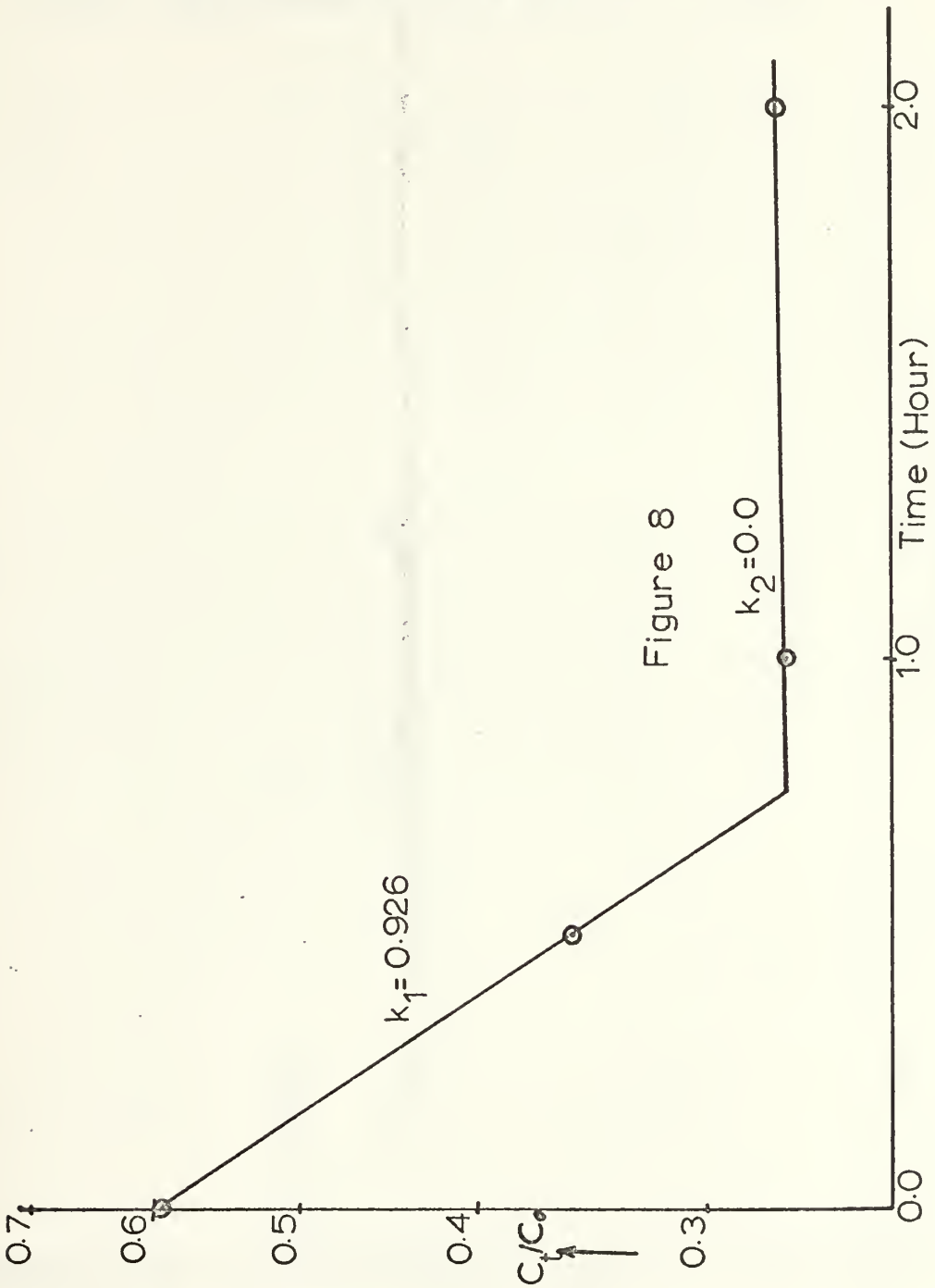


Figure 8

Acid-base titration analysis of products of 0.1 N Acetic acid oxidized at 250°C, 1500 psig

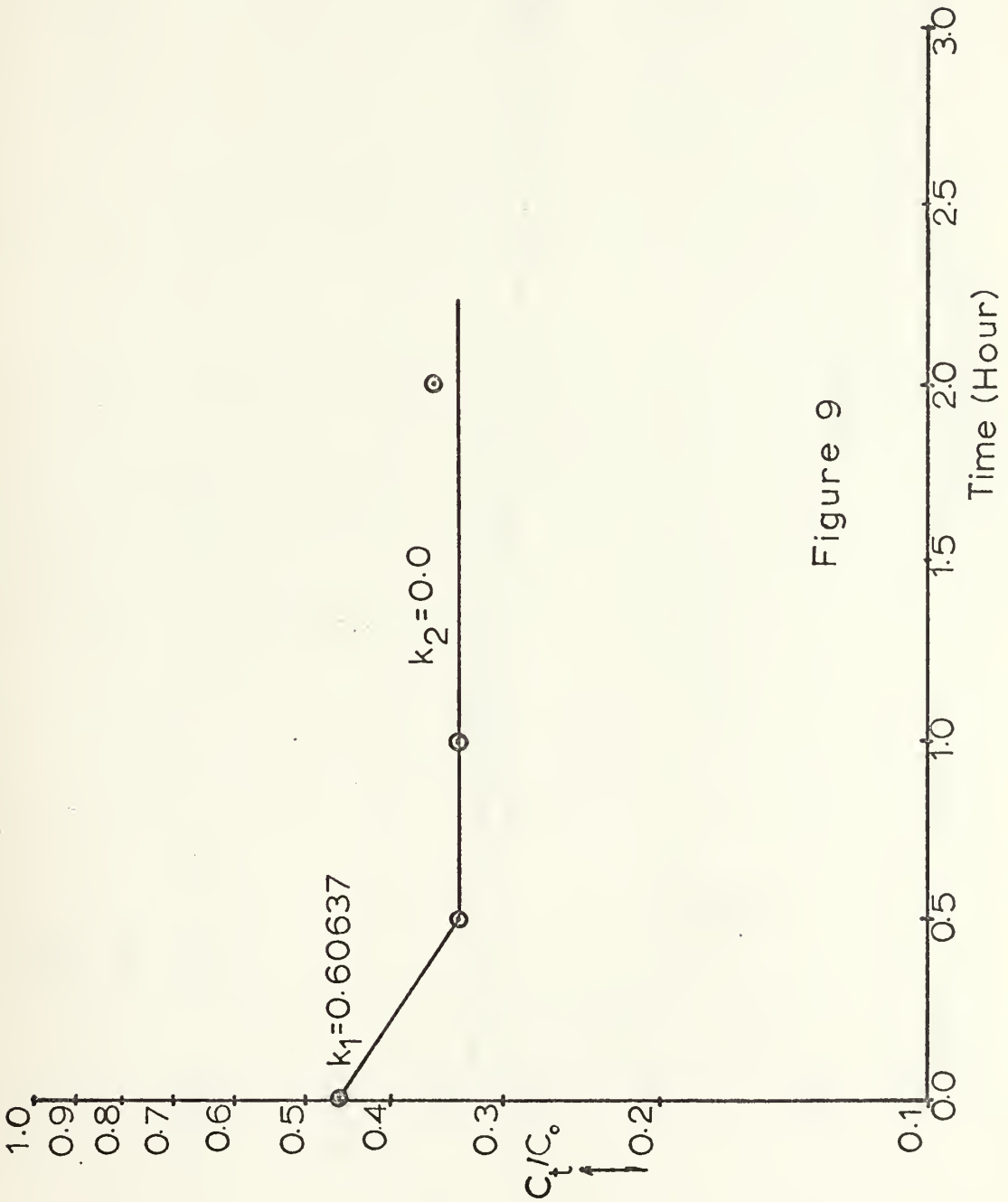


Figure 9

COD analysis of products of 0.1 N Acetic acid oxidized at 200°C, 1500 psig

Figure 10

GC analysis of products of 0.1 N Acetic acid oxidized at 200°C, 1500 psig

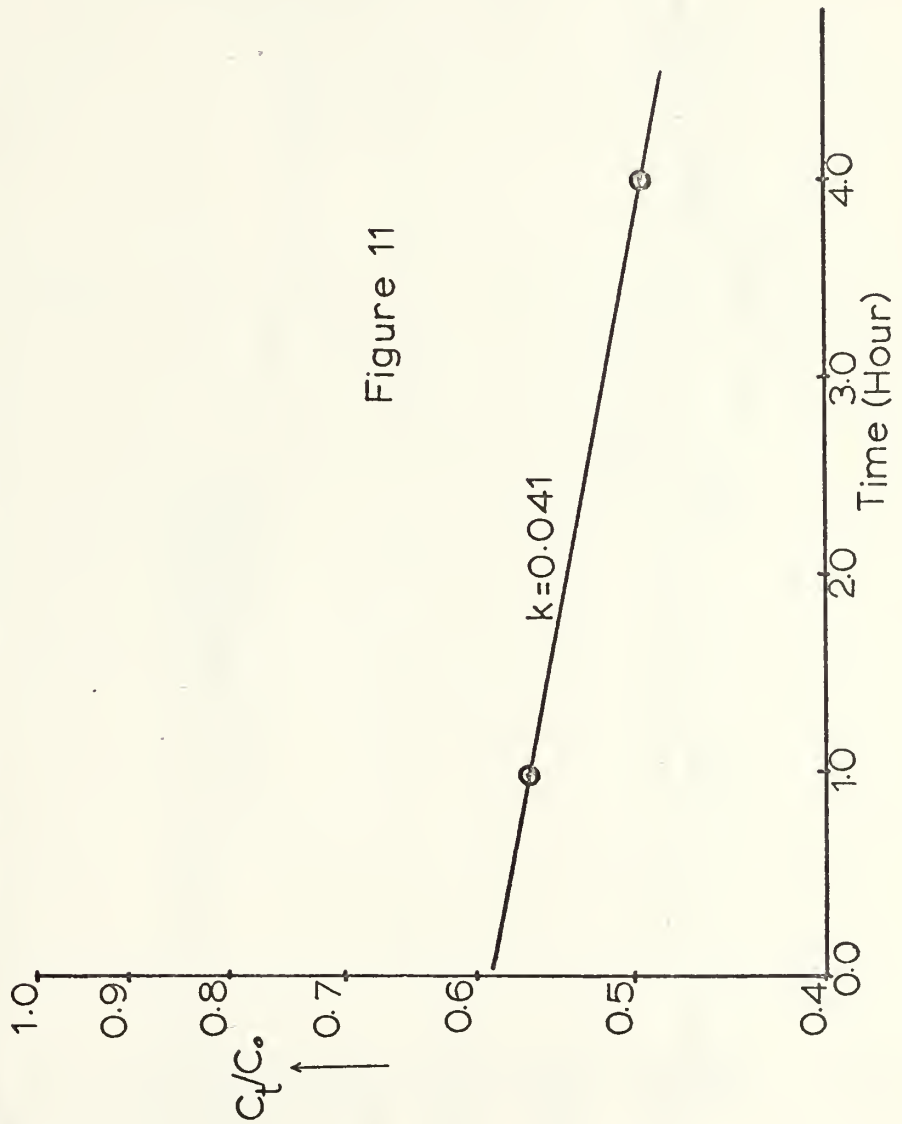


Figure 11

Acid base titration analysis of products of 0.1N Acetic acid oxidized at 200°C, 1500 psig

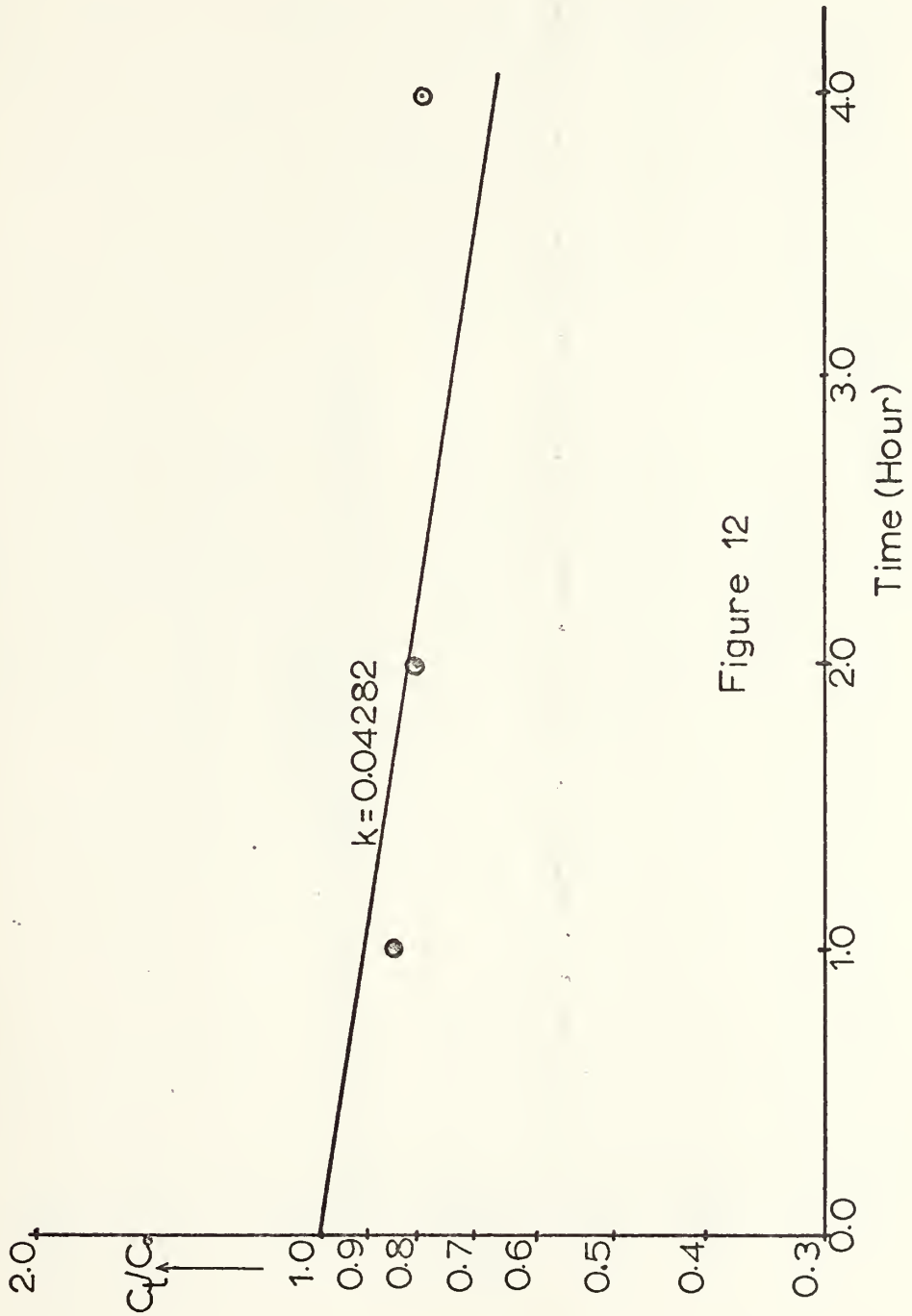


Figure 12

COD analysis of products of 0.1N Acetic acid oxidized at 200°C, 1000 psig

Figure 13

GC analysis of products of 0.1N Acetic acid oxidized at 200°C, 1000 psig

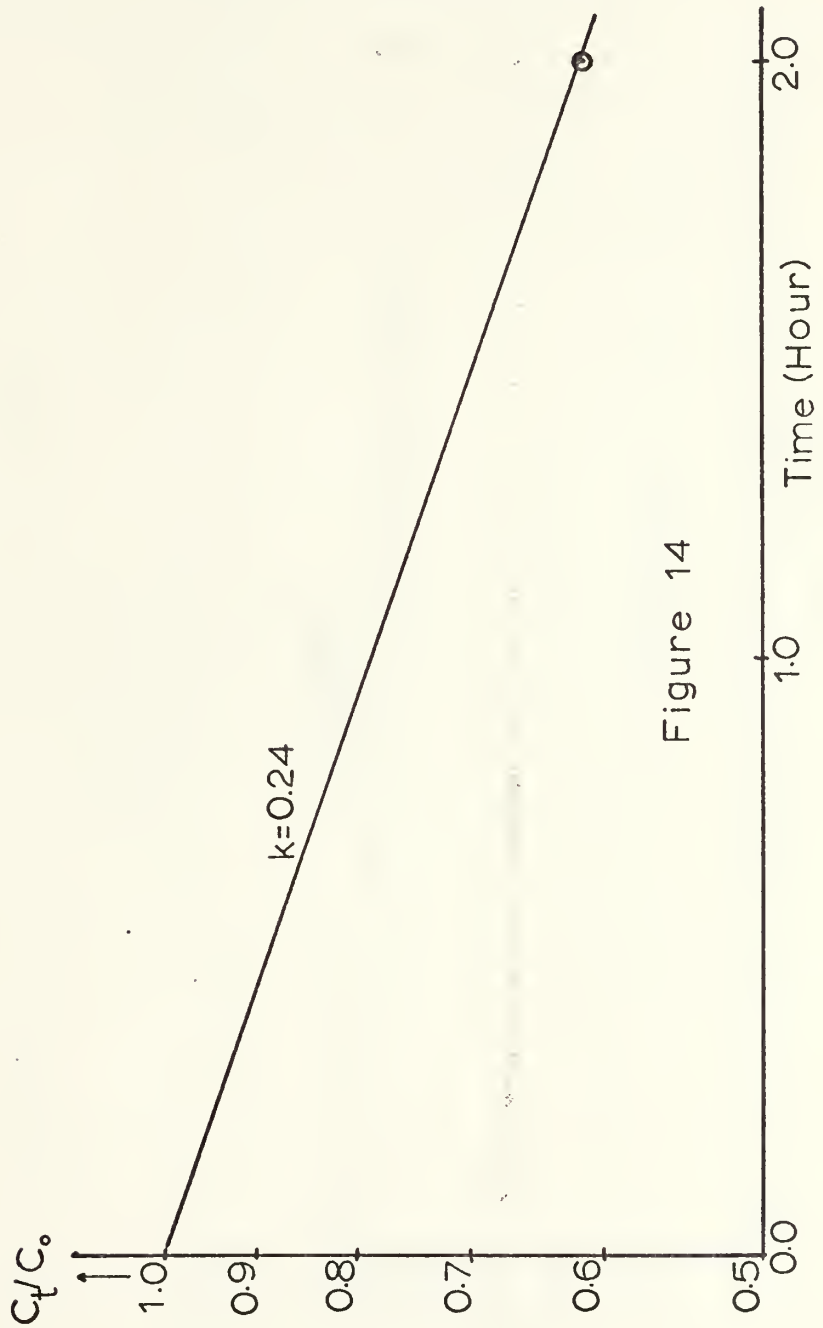


Figure 14

Acid base titration analysis of products of 0.1N Acetic acid oxidized at 200°C, 1000 psig

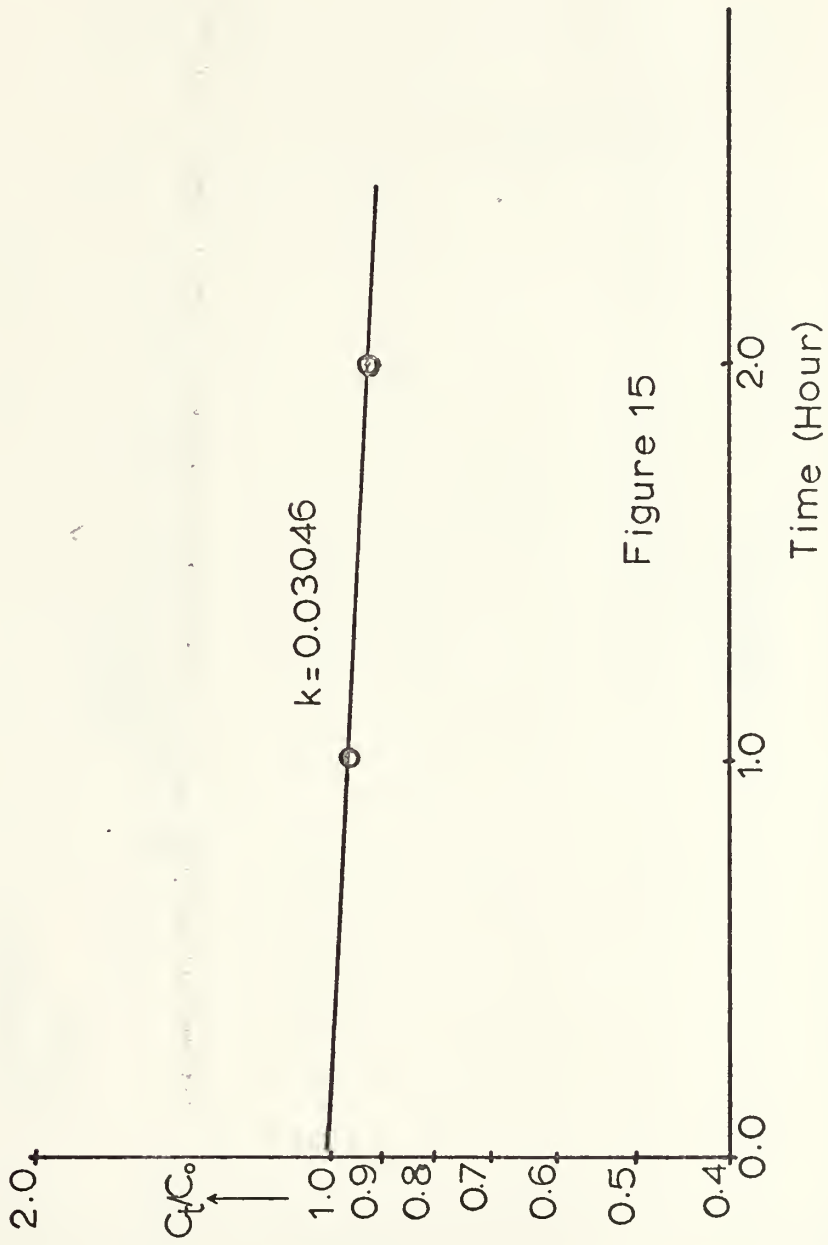


Figure 15

COD analysis of products of 0.05 N Acetic acid oxidized at 250°C, 1500 psig

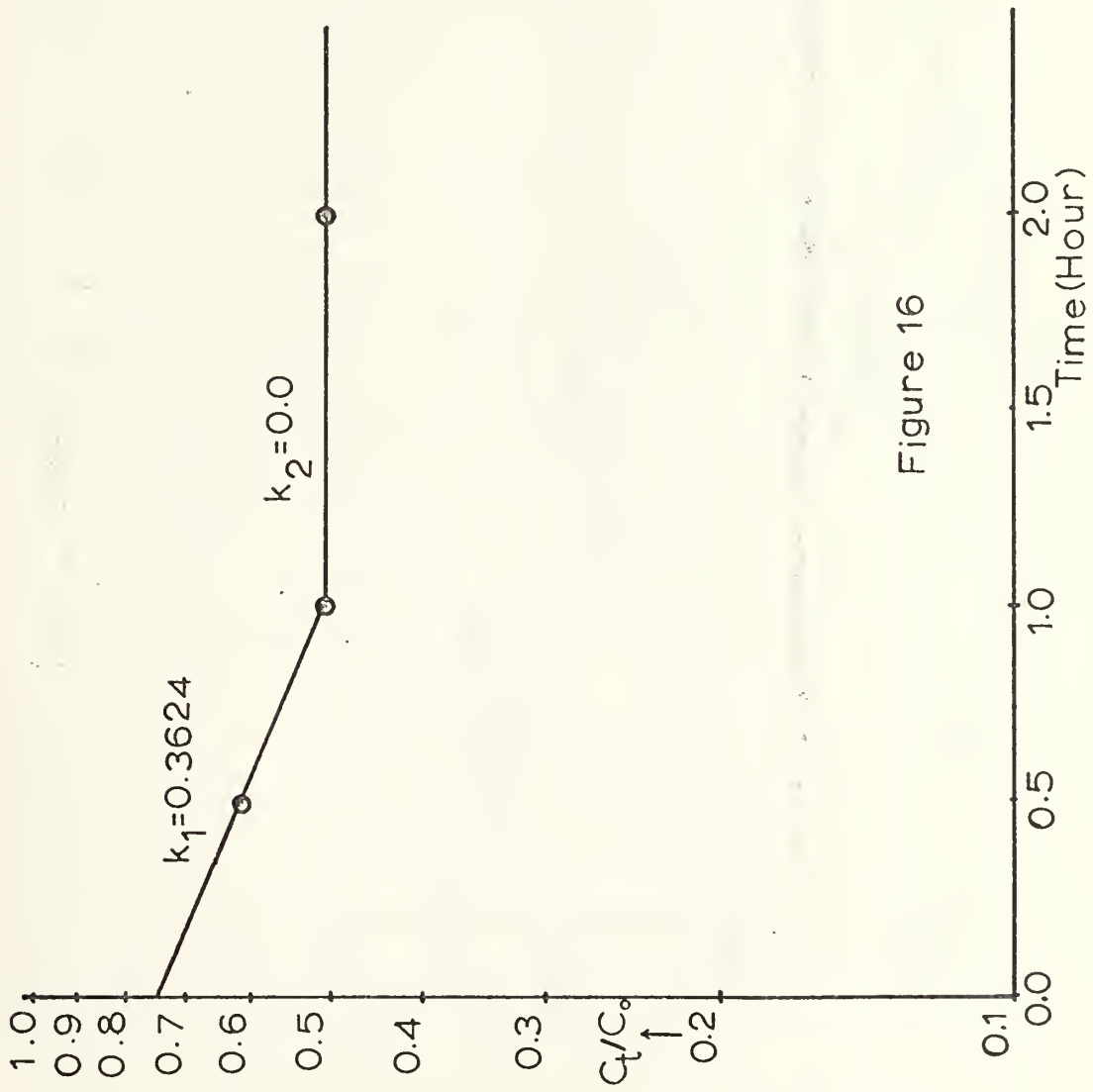


Figure 16

GC analysis of products of 0.05 N acetic acid oxidized at 250°C;1500 psig

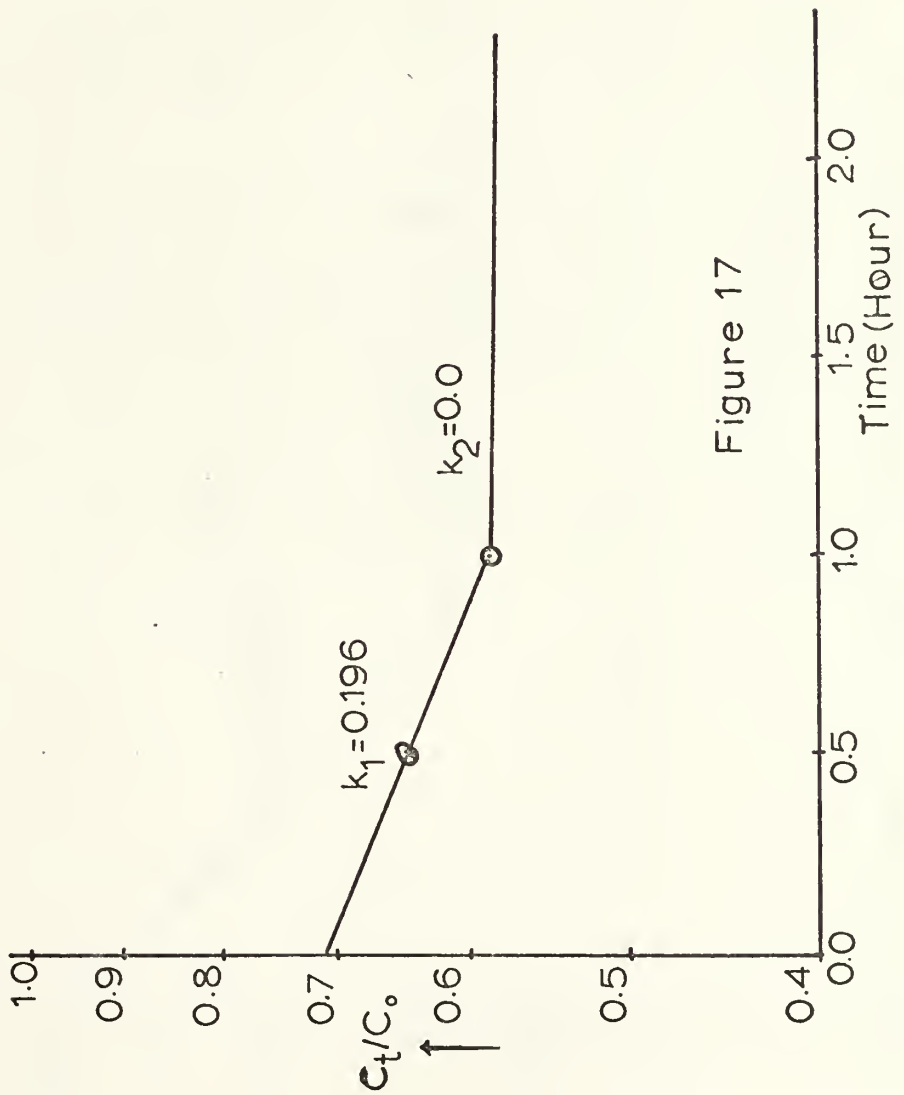


Figure 17

Acid base titration analysis of products of 0.05 N Acetic acid oxidized at 250 C, 1500 psig

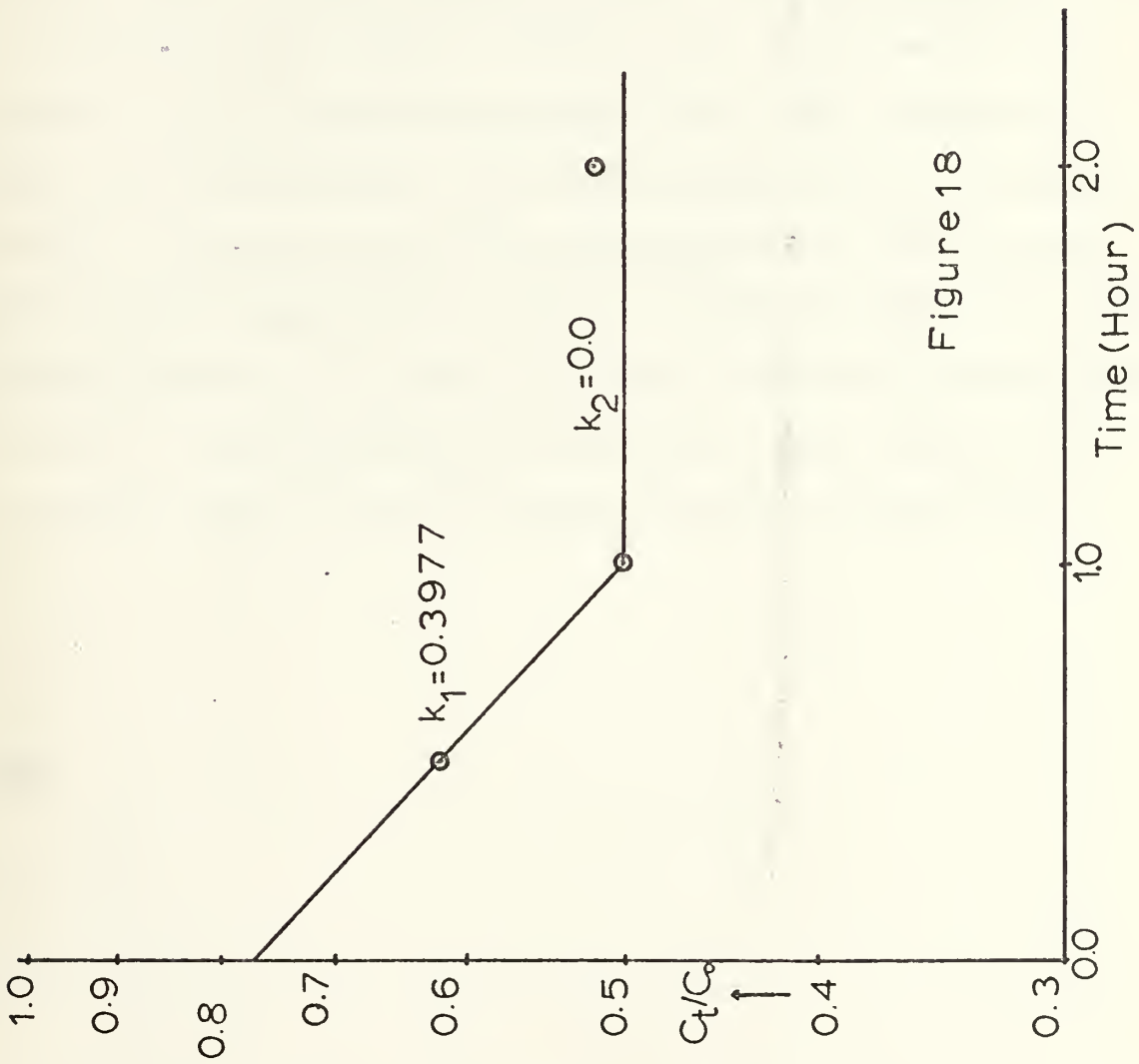


Figure 18

VI. SUMMARY

0.1 N and 0.05 N acetic acid solutions were prepared by diluting glacial acetic acid volumetrically. Oxidation reactions of those solutions were carried out with the selected reaction conditions of 200°C, 250°C and 1000 psig, 1500 psig for zero, one, two and in some cases four hours. 100 ml portions of solutions were placed into a one liter capacity stainless-steel reactor in a glass bottle, raised to temperature and shaken for each oxidation reaction. Reactions completed without catalysts did not show any oxidation at the end of several runs. Oxidation with the reaction conditions of 250°C under pressures of 1000 psig and 1500 psig gave much higher percentage than the condition of 200°C. Reactions under 250°C and 1000 psig design condition gave the oxidation values as high as 80% with catalyst after four hours. The chromel-constantan wire couple was put into solution butt welded together in order to produce potential for reduction of oxygen (elemental) to -2 oxidation state. Thus the oxidation of acetic acid was achieved.

VII. SUGGESTIONS FOR FURTHER WORK

Better and less cumbersome studies could be made if the reactor was modified to allow for sampling during the run, analysis of head gases and more detailed information to be gathered.

Automatic temperature control would make heat-up times less haphazard, overheating of initial reaction mixture less likely and operation closer to the critical point of water would be safer.

LIST OF REFERENCES

1. Andrulis, P.J. et al., "Aromatic Oxidation by Electron Transfer," Journal of the American Chemical Society, v. 88, p. 5473-5483, 1966.

2. Bartholomew, W. H., et al, "Oxyen Transfer and Agitation in Submerged Fermentations," Industrial and Engineering Chemistry, v. 42, No. 9, p. 1801-1809, September 1950.

3. Bawn, C. E. H. and Wright, T. K., "Oxidation of p-Toluic Acid Catalyzed by Cobalt Bromide," Discussions Faraday Society, v. 46, p. 164 1968.

4. Blattler, P. X., "Wet-Air Oxidation at Levittown", Water Sewage Works, v. 117, p. 32-34, 1970.

5. Brill, W. F., "Terephthalic Acid by Single-Stare Oxidation," Industrial and Engineering Chemistry, v. 52, No. 10, p. 837, 1960.

6. Brooks, R. B., "Heat Treatment of Activated Sludge," Water Pollution Control, p. 592-601, 1968.

7. Brooks, R. B. "Heat Treatment of Sewage Sludge," Water Pollution Control, p. 92-99, 1970.

8. Brooks, R. B. "Heat Treatment of Sewage Sludges," Water Pollution Control, p. 221-231, 1970.

9. Cifford, A. A. and Waters, W. A., "Oxidation of Organic Compounds by Cobaltic Salts, Part VI; Kinetic and Product Studies of the Oxidations of Some Carboxylic Acids," Journal of Chemical Society, p. 2796, 1965.

10. Cooper, C. M., Fernstrom, G. A. and Miller, S. A., "Performance of Agitated Gas-Liguid Contractors," Industrial and Engineering Chemistry, v. 36, p. 504-509, 1944.

11. Cooper, T. A., Clifford, A. A., Mills, D. J. and Waters, W. A., "Oxidation of Organic Compounds by Cobaltic Salts, Part VII," Journal of Chemical Society (B), p. 793, 1966.

12. Creighton, R. H. J., McCarthy, J. L. and Hibbert, H., "Aromatic Aldehydes from Spruce and Maple Woods," Journal of the American Chemical Society, v. 63, p. 312, 1941.

13. Creighton, R. H. J., McCarthy, J. L. and Hibbert, H., "Aromatic hydes from Plant Materials," ibid, p. 3049-3052, 1941.

14. Eckenfelder, W. W. Jr., "Process Design of Aeration Systems for Biological Waste Treatment," Chemical Engineering Progress, p. 286-296, July 1956.

15. Fassel, W. M. Jr., "Hyper-Atmospheric Extractive Metallurgy, Its Past, Present and Future," Pure and Applied Chemistry, v. 5, p. 683-699, 1962.

16. Fields, E. K. and Meyerson, S., Advanced Chemical Series, v. 76, p. 395, 1968.

17. Franke, N. W., Kiebler, M. W., Ruof, C. H., Sawich, T. R. and Howard, H. C., Industrial and Engineering Chemistry, v. 44, NO. 11, p. 2784-2792, November 1952.

18. Guccions, E., "Wet Combustion of Sewage Slodge Solves Disposal Problems," Chemical Engineering, p. 118-120, May 25, 1964.

19. Hoare, D. G. and Waters, W. A., "Oxidation of Organic Compounds by Cobaltic Salts, Part I: The Mechanism of Oxidation of Cyclohexanol and t-Butyl Alcohol," Journal of Chemical Society, p. 965, 1962.

20. Hoare, D. G. and Waters, W. A., "Oxidation of Organic Compounds by Cobaltic Salts, Part V:Kinetic and Product Studies, and Isotope Effects in the Oxidation of Secondary Alcohols," ibid, p. 2560, 1964.

21. Hammer, W. F., and Lloyd, S. J., Unit Processes in Organic Synthesis, 5 Th. Ed. Chapter. 13, Editted by P.H. Groggins, McGraw-Hill Book Co. Inc., New-York, 1958.

22. Hammond, G. S. and Cran, D. J., Organic Chemistry, McGraw-Hill Book Co. Inc., New-York, 1959.

23. Hay, A. S. and Blanchard, H. S., "Autoxidation Reactions Catalyzed by Cobalt Acetate Bromide," Canadian Journal of Chemistry, v. 43, p. 1306, 1965.

24. Heiba, E. I. et al., "Oxidations by Metal Salts V. Cobaltic Acetate Oxidation of Alkylbenzenes," Journal of the American Chemical Society, v. 91, p. 6830, 1969.

25. Hewson, W. B., McCarthy, J. L. and Hiebert, H., "The Mechanism of the Ethanolysis of Maple Wood at High Temperatures," Journal of the American Chemical Society, v. 63, p. 3048, November 1941.

26. Holtz, H. D., "Selectivity Differences of Some Cobalt Catalyzed Systems in the Liquid Phase Oxidation of Alkyl Aromatics," Journal of Organic Chemistry, v. 37, No. 13 p. 2069, 1972.

27. Howard, J. A. and Ingold, K. U., "Absolute Rate Constants for Hydrocarbon Autoxidation V.," Canadian Journal of Chemistry, v. 45, p. 785, 1967.

28. Howard, J. A. and Ingold K. U., "Absolute Rate Constants for Hydrocarson Autoxidation VI," ibid, p. 793, 1967.

29. Hurwitz, E. and Dundas, W. A., "Wet Oxidation of Sewage Sludge," Journal Water Pollution Control Federation, v. 32, No. 1, p. 918-929, September 1960.

30. Hurwitz, E., Teletzke, G. H. and Citchel, W. B., "Wet-Air Oxidation of Sewage Sludge," Water and Sewage Works, p. 298-305, August 1965.

31. Jenkins, S. H., "British Water Pollution Control," Environmental Science and Technology, v. 4, No. 3, p. 204-209, March 1970.

32. Kohnstam, G. and Williams, D. L. H., The Chemistry of Carboxylic Acids and Esters, p. 768, Edited by S. Patal, John Wiley & Sons Ltd., 1969.

33. Latimer, W. M., Oxidation Potentials, Second Ed. p. 38, Prentics Hall, Inc., New-York, 1952.

34. March, J., Advanced Organic Chemistry; Reactions, Mechanism and Structures, McGraw-Hill Book Co., 1968.

35. Marimoto, t. and Ogata, Y., "Kinetics of Autoxidation of Toluene Catalyzed by Cobaltic Acetate, Part I.," Journal of Chemical Society (B), p. 62, 1967.

36. Marimoto, T. and Ogata, Y., "ibid, Part II.," p. 1353, 1967.

37. Mitchell, J. S., "Presure Leaching and Reduction at the Carfield Rafinery," Mining Engineering, p. 1093-1095, November 1956.

38. Murdock, H. R., "Liquid Industrial Wastes... Pulp and Paper Industry" Industrial and Engineering Chemistry, v. 44, No. 33, p. 507-513, March 1952.

39. Norman, L. A., Organic Chemistry, Chapter. 23, Worth Publishers Company, 1971.

40. Onopohenko, A., Schltz, J. G. D. and Seekircher, Chemical Communications, p. 939, 1971.

41. Pearl, I. A., "Vanillin from Lignin Materials," Journal of the American Chemical Society, v. 64, p. 1429-1431, June 1942.

42. Pearl, I. A., "The Oxidation of Sulfite Spent Liquor With Cupric Oxide Under Pressure," ibid, v. 72, p. 2309, May 1950.

43. Pray, H. A., Schweickert, C. E. and Minnich, B. H.," Solubility of Hydrogen, Oxygen, Nitrogen and Helium in Water at Elevated Temperatures," Industrial and Engineering Chemistry, v. 44, NO. 5, p. 1146-1151, May 1952.

44. Reeve, D. A. D., "Study Tour of Sewage-Treatment Installations and Research Centers in the U.S.A., Japan, Switzerland and Germany," Water Pollution Control, v. 70, No. 6, 662-667, 1971.

45. Ravens, D. A. S., "The Kinetics and Mechanism of the Autoxidation of p-Toluic Acid in Acetic Acid Solution Catalysed by Cobalt and Maganese Bromides," Transactions of Faraday Society, v. 55, p. 1768, 1959.

46. Shreve, R. H., The Chemical Process Industries, Second Ed., p. 44, McGraw-Hill Book Co., Inc. New-York, 1956.

47. Smith, R. C., Tomarelli, R. C. and Howard, H. C., "Oxidation of Carbonaceous Materials to Organic Acids by Oxygen at Elevated Pressures," Journal of the American Chemical Society, v. 61, p. 2398-2402, September 1939.

48. Sakota, K., Kamiya, Y. and Ohta, N., "Aromatic Oxidation by Cobaltic Acetate in Acetic Acid," Canadian Journal of Chemistry, v. 47, p. 387, 1969.

49. Sato, T. and Akiyama, T., "Biochemical Oxidation of Volatile Organic Acids by Activated Sludge," Water Research, v. 6, p. 1059-1072, 1972.

50. Scott, E. J. Y., "The Kinetics of the Reactions of Cobalt (II) and Cobalt (III) Acetates with Benzyel Hydroperoxide in Acetic Acid at 25°C," Journal of Physical Chemistry, v. 74, p. 1174, 1970.

51. Swanwick, J. D., "Recent Developments in Sludge Technology in the U.S.A.." Water Pollution Control, p. 374-390, 1968.

52. Teletzke, G. H., "Wet Air Oxidation," Chemical Engineering Progess, v. 60, No. 1, p. 33-38, January 1964.

53. Teletzke, G. H., "Wet Air Oxidation of Sewage Sludge," Process Biochemistry, p. 329-332, September 1966.

54. Teletzke, G. H., et al, "Components of Sludge and Its Wet-Air Oxidation Products," Journal Water Pollution Control Federation, v. 39, No. 6, p. 994-1005, June 1967.

55. Walling, C., Free Radicals in Solutions, p. 360-370, Wiley, New-york, 1957.

56. Walling, C., "Limiting Rates of Hydrocarbon Autoxidations," Journal of the American Chemical Society, v. 91, p. 7590, December 31, 1969.

57. Warrick, L. F., "Industrial Wastes... Pulp and Paper Industry," Industrial and Engineering Chemistry, v. 39, No. 5, p. 670-676, May 1947.

58. Woodward, A. E. and Mesrobian, R. B., "Low Temperature Autoxidation of Hydrocarbons," Journal of the American Chemical Society, v. 75, p. 6189, 1953.

59. Van Halden, R. et al., "The Autoxidation of Isopropylbenzens to Benzoic Acids in Acid Media, II. The Attack at the Alkyl Group," Recrueil, v. 80, p. 1237, 1961.

60. Van Halden et al., ibid, p. 1257.

61. Zimmermann, F. J., "New Waste Disposal Process," Chemical Engineering, p. 117-120, August 25, 1958.

INITIAL DISTRIBUTION LIST

		No. Copies
1.	Defense Documentation Center Cameron Station Alexandria, Virginia 22314	2
2.	Library, Code 0212 Naval Postgraduate School Monterey, California 93940	2
3.	Assoc. Professor C.F. Rowell, Code 61Rw (Thesis Advisor) Department of Physics and Chemistry Naval Postgraduate School Monterey, California 93940	2
4.	Dz.Kd.Ütgm. Yakup Üner, Turkish Navy (Student) Dz. Hrb. OK. K.liği Öğretim Üyesi Heybeliada, ISTANBUL - TURKEY	1
5.	Middle East Technical Üniversity The Library Ankara - TURKEY	2
6.	Deniz Harb Okulu Kütüphanesi Heybeliada - ISTANBUL TURKEY	2
7.	Deniz Harb Akademisi Kütüphanesi Yildiz - ISTANBUL TURKEY	3
8.	Boğaziçi Üniversitiesi The Library ISTANBUL - TURKEY	2

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Naval Postgraduate School
Monterey, California 93940

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP

3. REPORT TITLE

The Mechanism of High Pressure Oxidations of Aliphatic Acids

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Master's Thesis; June 1973

5. AUTHOR(S) *(First name, middle initial, last name)*

Yakup Oner

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
June 1973	64	61

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

Approved for Public Release; Distribution Unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Naval Postgraduate School Monterey, California 93940

13. ABSTRACT

As a part of the study of the mechanism of high pressure oxidation of aliphatic acids, acetic acid solutions of 0.1 and 0.05 Normality were oxidized. Reaction conditions were selected as 200° -- 250°C, and 1000 - 1500 psig for zero, one-half, one, two and four hour oxidation periods. No oxidation was observed at the end of several reactions without a catalyst. As high as 80% oxidation was observed from the oxidation for four hours at 250°C under 1500 psig of total pressure with Chromel-Constantan thermocouple wire (15 cm) as catalyst in the reacting solution. Increasing temperature showed an increasing reaction rate, while increases in pressure and decreases in concentration showed a decreasing effect on the reaction rate.

DD FORM 1 NOV 68 1473 (PAGE 1)
S/N 0101-807-6811

UNCLASSIFIED
Security Classification

A-31408

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
High Pressure Oxidation						
Oxidation of Aliphatic Acids						
High Pressure Oxidation of Acetic Acid						
Free Radical Reactions						

Thesis
05815 Oner
c.1

145034

The mechanism of high pressure oxidations of aliphatic acids.